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Report on the 11th inter-laboratory comparison organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons

Four marker PAHs in spiked olive oil

Stefanka Bratinova, Philippe Verlinde and Thomas Wenzl

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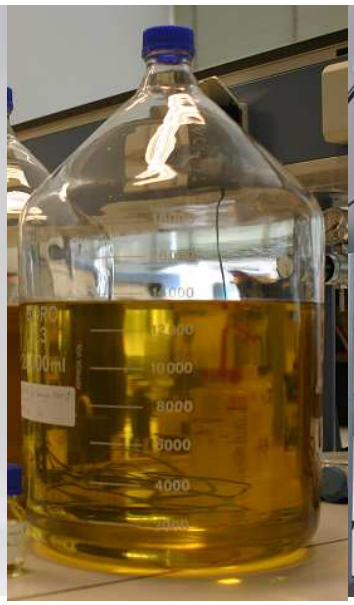

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1. Executive summary

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of fused aromatic rings; some of them are carcinogenic and mutagenic. Humans are exposed to PAHs via air and drinking water, but mostly by intake of food. To protect the wellbeing of consumers EU legislation introduced maximum levels for certain PAHs in food.

European Union food safety legislation created EU and national reference laboratories, which should contribute to a high quality and uniformity of analytical results. This objective can be achieved by activities such as the application of validated analytical methods, ensuring that reference materials are available, the organisation of comparative testing and the training of staff from laboratories.

This report presents the results of the eleventh inter-laboratory comparison (ILC) organised by the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons (EU-RL PAHs) on the determination of the four EU marker PAHs, benz[*a*]anthracene (BAA), benzo[*a*]pyrene (BAP), benzo[*b*]fluoranthene (BBF) and chrysene (CHR), in olive oil spiked with 15+1 EU priority PAHs. It was conducted in accordance with ISO Standard 17043 and the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.

In agreement with National Reference Laboratories (NRLs), the test material used in this exercise was commercial olive oil spiked with 15 + 1 EU priority PAHs. The spiked oil was prepared gravimetrically and values obtained from preparation were used to benchmark the results reported by participants.

Both officially nominated NRLs and official food control laboratories of the EU Member States were admitted as participants.

The participants were free to choose the method of analysis. The four EU marker PAHs were chosen as target analytes as limits for their sum were recently introduced in European legislation. The performance of the participating laboratories in the determination of the target PAHs in olive oil was expressed by both z-scores and zeta-scores. Those scores provide a normalised performance evaluation to make proficiency test (PT) results comparable. Laboratories complying with the PT scheme's fitness for purpose criterion will commonly produce scores falling between - 2 and 2. The gravimetrical preparation concentrations, corrected for the purity of the reference materials were applied as assigned values for the proficiency assessment. The uncertainties of the assigned values were calculated taking into account the purity of the reference materials used and the weighing operation carried-out.

Participants also received a solution of PAHs in the solvent of their choice (either toluene or acetonitrile) with known PAH content for the verification of their instrument calibration.

This proficiency testing round has demonstrated the high competence of all participating laboratories in the analysis of regulated PAHs in an oily matrix. More than 90 % of the reported test results were graded with z-scores that were less than an absolute value of 2, indicating good agreement with the assigned reference values of the test material.

2. Introduction

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Directorate General Joint Research Centre hosts the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (EU-RL-PAH). One of its core tasks is to organise inter-laboratory comparisons (ILCs) for the National Reference Laboratories (NRLs) [i, ii].

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found in the environment. In food, PAHs may be formed during industrial food processing and domestic food preparation, such as smoking, drying, roasting, baking, frying, or grilling.

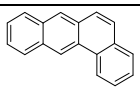
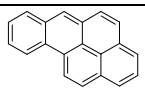
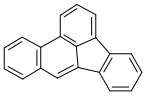
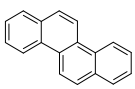
In 2002 the European Commission Scientific Committee on Food identified 15 individual PAHs as being of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene (BAP) as a marker for a "total-PAH content" [iii]. The toxicological importance of these compounds was confirmed in October 2005 by the International Agency for Research on Cancer (IARC), which classified BAP as carcinogen to human beings (IARC group 1), cyclopenta[*cd*]pyrene - CPP, dibenzo[*a,h*]anthracene - DHA, and dibenzo[*a,l*]pyrene - DLP as probably carcinogenic to human beings (group 2a), and nine other EU priority PAHs as possibly carcinogenic to human beings (group 2b) [iv].

As a consequence, the European Commission (EC) issued Commission Regulation (EC) No 1881/2006 setting maximum levels of benzo[*a*]pyrene in food, Commission Regulation (EC) No 333/2007 laying down sampling methods and performance criteria for methods of analysis for the official control of benzo[*a*]pyrene levels in foodstuffs, and Commission Recommendation 2005/108/EC on the further investigation into the levels of PAHs in certain foods [v, vi, vii].

To evaluate the suitability of BaP as a marker for occurrence and toxicity of PAHs in food, the European Commission asked the European Food Safety Authority (EFSA) for a review of the previous risk assessment on PAHs carried by the Scientific Committee on Food (SCF).

The scientific opinion on polycyclic aromatic hydrocarbons in food was published by EFSA in June 2008 [viii]. EFSA concluded that benzo[*a*]pyrene was not a suitable indicator for the occurrence of PAHs in food and that four (PAH4) or eight PAHs (PAH8) were more suitable indicators for the occurrence of PAHs in food. However, PAH8 does not provide much added value compared to PAH4. Following these conclusions the Standing Committee on the Food Chain and Animal Health agreed to base risk management measures on four PAHs (PAH4) - BAA, BAP, BBF, and CHR. However, maximum levels for BAP would be maintained to ensure comparability with historical data. In the following the PAH4 will be also indicated as "the four EU marker PAHs". They are listed in **Table 1.** A maximum level for the sum of the four PAHs was included in the amendment of Commission Regulation (EC) No 1881/2006 [vi]. Coherently, also Commission Regulation (EC) No 333/2007 [vii] which lays down minimum method performance criteria was revised by Commission Regulation (EC) No 836/2011.

Table 1: Names and structures of the four EU marker PAHs.

1	**Benz[*a*]anthracene (BAA)**		**2**	**Benzo[*a*]pyrene (BAP)**	
3	**Benzo[*b*]fluoranthene (BBF)**		**4**	**Chrysene (CHR)**	

3. Scope

As specified in Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules [ii], one of the core duties of EU-RLs is organising inter-laboratory comparison tests (ILCs).

This inter-laboratory comparison study aimed to evaluate the measurement capabilities of the National Reference Laboratories (NRLs) and EU official food control laboratories (OCLs) for the four EU marker PAHs in olive oil. The appropriateness of the reported measurement uncertainty was also tested as this parameter is important in the compliance assessment of food with EU maximum levels.

The ILC was designed and evaluated according to ISO Standard 17043:2010. [ix].

4. Participating Laboratories

Officially nominated NRLs and OCLs of the EU Member States were admitted as participants. The participants are listed in **Table 2** and **Table 3** respectively.

Table 2: List of participating National Reference Laboratories

Institute	*Country*
AGES - Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	AUSTRIA
Scientific Institute of Public Health	BELGIUM
SGL - State General Laboratory, Environmental and other Food Contamination Laboratory	CYPRUS
Nàrodní referenční laboratoř pro polycyklické aromatické uhlovodíky - Státní veterinární ústav Praha	CZECH REPUBLIC
Division of Food Chemistry, National Food Institute, Technical University of Denmark	DENMARK
Food and Vet. Administration in Aarhus	DENMARK
Tartu Laboratory of Health Protection Inspectorate	ESTONIA
EVIRA - Finnish Food Safety Authority	FINLAND
LABERCA - Laboratoire d'Etude des Résidus et des Contaminants dans les Aliments	FRANCE
BVL - Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	GERMANY
GCSL - General Chemical State Laboratory - Food Division - Laboratory	GREECE
Food Chain Safety Office, Food & Feed Safety Directorate, Food Toxicological NRL.	HUNGARY
The Public Analyst's Laboratory Dublin	IRELAND
Istituto Superiore di Sanità	ITALY
BIOR - Institute of Food Safety, Animal Health and Environment	LATVIA
National Veterinary Laboratory (National Food and Veterinary Risk Assessment Institute)	LITHUANIA
Laboratoire National de Santé, Contrôle Alimentaire	LUXEMBOURGE
RIKILT- Institute of Food Safety	THE NETHERLANDS
NIFES - National Institute of Nutrition and Seafood Research	NORWAY
National Institute of Public Health - National Institute of Hygiene	POLAND
SVUPUDK - State Veterinary and Food Institute Dolný Kubín	SLOVAKIA
Zavod za zdravstveno varstvo Maribor	SLOVENIA
AESAN - Centro Nacional de Alimentaciòn (Spanish Food Safety and Nutrition Agency)	SPAIN
National Food Agency	SWEDEN
FERA - The Food and Environment Research Agency	UNITED KINGDOM

All the registered 25 NRL's sent the results.

Table 3: List of participating Official Food Control Laboratories

Institute	*Country*
ANALYTEC	AUSTRIA
Institut Dr. Wagner	AUSTRIA
Umweltinstitut des Landes Vorarlberg	AUSTRIA
State Veterinary Institute Olomouc	CZECH REPUBLIC
STATE VETERINARY INSTITUTE JIIHLAVA	CZECH REPUBLIC
Health Board - Tallin	ESTONIA
LDA 22	FRANCE
Laboratoire Departemental de la Sarthe	FRANCE
CVUA-MEL	GERMANY
Chemisches Untersuchungsamt der Stadt Hagen	GERMANY
Arpa Puglia	ITALY
ASL Milano	ITALY
NVWA	THE NETHERLANDS
State Veterinary and Food Institution Kosice	SLOVAKIA
State Veterinary and Food Institution Bratislava	SLOVAKIA
LABORATORIO DE SALUD PÚBLICA DE MADRID	SPAIN
CENTRO DE SALUD PÚBLICA DE ALICANTE	SPAIN

All the 17 registered OCLs reported results.

5. Time frame

The ILC was agreed with the NRLs at the EU-RL PAH workshop in Geel on the 25th of April 2012. It was announced on the IRMM web page (see ANNEX 1) and invitation letters were sent to the laboratories on the 28th of September 2012 (see ANNEX 2). Test samples were dispatched (see ANNEX 3) on the 7th of November 2012 and the deadline for reporting of results was set to the 4th of January 2013.

The documents sent to the participants are presented in ANNEX 4.

6. Confidentiality

The identities of participants are kept confidential unless the participant provides a letter of consent to the PT organiser giving permission to disclose his/her details and results to a third party.

7. Test materials

7.1 Preparation

The test materials of this PT round was olive oil spiked with 15+1 EU priority PAHs, in the following denoted as OIL. This matrix represents the food category 6.1.1 "Oils and fats, intended for direct human consumption or use as an ingredient in food" specified in Commission Regulation (EC)

No 835/2011, with a maximum level for BAP and for the sum of the four PAHs (in the following indicated as SUM) of 2.0 µg/kg and 10.0 µg/kg respectively.

Participants also received a solution of the four EU Priority PAHs in either acetonitrile or toluene (according to their choice, see ANNEX 3) with disclosed concentrations, which allowed them to check their instrument calibration against an independent reference. The technical specifications are provided in Annex 5.

The test material was prepared at the EU-RL PAH laboratories from four liters of olive oil, checked for absence of PAHs prior to the test material preparation. It was spiked with a PAH standard solution containing besides the four EU marker PAHs also other the other PAHs mentioned by the European Commission Scientific Committee on Food. The standard solution was prepared from neat certified reference materials (purchased from BCR®, Institute for Reference Materials and Measurements, Geel, Belgium, except CPP - purchased from Biochemisches Institut für Umweltkarzinogene, Großhansdorf, Germany, BCL - purchased from Dr. Ehrenstorfer, Germany, and DIP - purchased from Campro Scientific, Germany). Single standard stock solutions of each analyte were produced by substitution weighing of neat substance on a microbalance and dissolution in toluene. These standard stock solutions were mixed and diluted further gravimetrically with toluene to obtain the solution used for spiking the olive oil. After spiking, the test sample was homogenised over night by intensive stirring. Portions of about 20 g spiked olive oil test material were sealed under inert atmosphere in 25 ml amber glass ampoules.

7.2 Homogeneity and stability

Homogeneity of the olive oil test sample was evaluated according to ISO Standard 13528. Ten ampoules of the olive oil test material were selected randomly and analysed by online-donor acceptor complex chromatography high performance liquid chromatography with fluorescence detection. The test material was rated sufficiently homogeneous (see ANNEX 6).

The stability of the test materials was evaluated by analysing the test material after the deadline for reporting of results. Significant differences of the analyte contents between the analysis results and the preparation concentrations were not found. Hence stability of the samples over the whole study period was assumed.

7.3 Assigned value and standard deviation for proficiency assessment

The gravimetrical preparation concentrations, corrected for the purity of the reference materials were applied as assigned values for the proficiency assessment. The assigned values of the target PAHs are listed in **Table 4.**

The uncertainties of the assigned values were calculated taking into account the purity of the reference materials used and the weighing operation carried-out according to GUM [*x*].

The standard deviation for proficiency assessment, σ_P, was set for the individual analyte equal to the maximum tolerable uncertainty (Uf), which is calculated according to Equation 1 [xii]. A LOD value of 0.30 µg/kg, and α equal to 0.2 were applied for this purpose. The standard deviation for proficiency testing was calculated for the SUM parameter from the σ_P - values of the individual analytes applying the law of uncertainty propagation.

Equation 1 $$U_f = \sqrt{(\mathrm{LOD}/2)^2 + (\alpha \mathrm{C})^2}$$

where U_f relates to the maximum tolerated standard measurement uncertainty, LOD to the limit of detection, α to a numeric factor depending on the concentration C as given in Commission Regulation (EC) No 836/2011.

Table 4: Analyte contents of the olive oil test material

		Assigned value*	U	σ_P	
Analyte	**Analyte short name**	**µg/kg**	**µg/kg**	**µg/kg**	**%**
Benz[*a*]anthracene	BAA	2.79	0.02	0.58	20.7
Benzo[*a*]pyrene	BAP	2.27	0.03	0.48	21.1
Benzo[*b*]fluoranthene	BBF	5.32	0.05	1.07	20.2
Chrysene	CHR	2.77	0.03	0.57	20.7
Sum of the four marker PAHs	SUM	13.15	0.07	1.43	10.9

* gravimetrical preparation concentration of the material for the individual analytes, respectively sum of the individual concentrations for the SUM parameter

σ_p standard deviation for proficiency assessment.

U expanded uncertainty of the assigned value (k=2). For the individual analytes the standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of the test material; for the SUM is equal to the combined standard uncertainty of the four analytes.

8. Design of the proficiency test

The design of the PT foresaw triplicate analyses of the test sample and reporting of the individual results of replicate analyses for the single analytes, in the following denoted as OIL_REP. Additionally a "value for proficiency assessment", in the following denoted as "final value - OIL_FIN", was requested for both the single analytes and the sum of the four PAHs. Both OIL_REP results and OIL_FIN results had to be reported corrected for recovery (and recovery had to be stated in the questionnaire together with other parameters of the method applied); OIL_FIN results had also to be accompanied by the respective expanded measurement uncertainty (with a coverage factor of 2). The OIL_FIN results were the values used for performance assessment.

Participants were asked to report besides analysis results also details of the applied analysis method (see ANNEX 7).

Each participant received at least one ampoule of a solution of the target PAHs in the chosen solvent (2 ml), with disclosed content, and at least one ampoule of OIL (20 ml).

9. Evaluation of Laboratories

9.1 General

The results reported by participants are listed in ANNEX 8. In case the coverage factor k was not reported by the participant, a coverage factor of two was assumed (see the Outline in ANNEX 4).

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the olive oil test material, which was expressed by z-scores but zeta-scores were calculated as well considering the uncertainty of the test results as estimated by each participant.

9.2 Evaluation criteria

z-Scores

z-Scores were calculated based on the OIL_FIN values. Equation 2 presents the formula for calculation of z-scores.

Equation 2 $$z = \frac{\left(x_{lab} - X_{assigned}\right)}{\sigma_P}$$

where z refers to the z-score, x_{lab} to the reported "value for proficiency assessment", $X_{assigned}$ to the assigned value, and σ_P to the standard deviation for proficiency testing.

zeta-Scores

In addition to z-scores, zeta-scores were calculated. In contrast to z-scores, zeta-scores describe the agreement of the reported result with the assigned value within the respective uncertainties. zeta-Scores were calculated according to Equation 3.

Equation 3 $$zeta = \frac{x_{lab} - X_{assigned}}{\sqrt{u_{lab}^2 + u_{assigned}^2}}$$

where *zeta* refers to the zeta-score, x_{lab} to the reported "final value", $X_{assigned}$ to the assigned value, u_{lab} to the standard measurement uncertainty of the reported result, and $u_{assigned}$ to the standard uncertainty of the assigned value.

Whenever uncertainty was not reported by the laboratory, the corresponding zeta-score was not calculated.

Unsatisfactorily large zeta-scores might be caused by underestimated measurement uncertainties, large bias, or a combination of both. On the contrary, satisfactory zeta scores might be obtained even with high bias if the uncertainty is sufficiently high. However, legislation specifies maximum tolerable standard uncertainties. Uncertainties exceeding them are not considered fit-for-purpose. Therefore, the uncertainties reported by the participants for the four PAHs were checked whether they comply with the thresholds provided by the "fitness-for-purpose" function. The results reported by the participants and the maximum tolerated LOD of 0.3 µg/kg were applied for the calculation of respective threshold values. For the SUM parameter the agreement between reported standard measurement uncertainties and the combined standard uncertainty of the four EU marker PAHs was evaluated. The latter was derived via the law of error propagation from the uncertainties reported for the individual analytes. Non-compliant reported uncertainties are highlighted in Table 5 and Table 6.

The performance of the laboratories was classified according to ISO/IEC 17043:2010 [ix]. Following scheme is applied for the interpretation of zeta scores and z-scores:

$|score| \leq 2.0$ = satisfactory performance
$2.0 < |score| < 3.0$ = questionable performance
$|score| \geq 3.0$ = unsatisfactory performance

9.3 Evaluation of results

The participants were requested to report for the four analytes the results of replicate measurements and a "value for proficiency assessment" (OIL_FIN), which is the result they wish to be applied for the calculation of performance indicators. z-Scores and zeta-scores were attributed only to these results. The individual results of replicate analyses were not rated.

Each laboratory had to report a total of 17 results (12 results for replicate measurements plus 5 values for proficiency assessment), therefore the reported number of results of registered participants was 714. The 42 participants in the study reported in total 698 results. One participant reported only value for proficiency assessment without replicates and another participant reported only two replicates and value for proficiency assessment.

About 94.4 % and about 90.5 % of the results reported from NRLs and OCLs respectively obtained a satisfactory z-score.

In Figures 1 and 2 overviews of the z-scores assigned to the results are given for NRLs and OCLs respectively. The larger the triangles, the larger were the differences to the assigned values. Red triangles indicate z-scores above an absolute value of three, whereas yellow triangles represent z-scores in the questionable performance range. For questionable and unsatisfactory scores, the corresponding score values are presented next to the triangles. The three non-satisfactory results of NRLs were reported by two participants; whereas in the case of OCLs the three non-satisfactory results were reported by one laboratory. The questionable results are in total 10.

The numerical values of the calculated z-scores are compiled in **Table 5** for NRLs and OCLs respectively. z-Scores with an absolute value of above 2 are highlighted in red.

Table 6 presents the respective zeta-scores. As for the z-scores, data outside the satisfactory performance range are highlighted in red. The assessment of the performance of the participants based on the reported measurement uncertainty gave a less favourable picture. Only 78.4% and 77.6% respectively (for NRLs and OCLs) of the zeta-scores calculated for the four individual analytes and the SUM are within the range given by $|zeta| \leq 2$. It has to be noted that the absolute value of the zeta-scores were for many participants much higher than the z-scores attributed to the same results. Consequently the laboratories perform according to internationally agreed standards, which form the basis for the z-scores, but seem to have partially difficulties in calculating realistic measurement uncertainty values. The establishment of proper measurement uncertainty values caused problems especially for the SUM parameter. The majority of participants reported for this parameter measurement uncertainty values different from the value which is derived by the law of uncertainty propagation.

Hence the EU-RL PAHs will continue to pay special attention to this parameter, in the ILCs to come, as it has major implications on the assessment of compliance of food with European legislation.

The graphical representations of the distribution of results for the individual analytes are given in ANNEX 8 together with the results of replicate analyses and Kernel density plots. Data are presented as reported by the participants.

For each analyte the figure shows the individual analysis results of the three replicate determinations. The assigned value is shown as green dotted line. The blue boxes represent the expanded uncertainties reported by participants for the "value for proficiency assessment". The arithmetic mean of the results of the individual participant is indicated in the blue boxes by a blue line. The red dotted lines represent deviations from the assigned value of $\pm 2\sigma_{p.}$

As could be seen from the Kernel density plots the distribution of results for each analyte and for the sum of the analytes were close to a Gaussian distribution. The robust mean and the mode are very close to the assigned (reference) value, which demonstrates that the analysis was not biased.

The figures in ANNEX 9 are an aid to allow laboratories to compare the performance of their method to those of other participants with respect to bias (closeness to the assigned value, plotted on the x-axis) and precision (the standard deviation for repeatability, plotted on the y-axis). A vertical solid green line depicts the assigned value; laboratories are represented by blue dots (mean value of the replicates and the associated standard deviation of the replicates). The light blue area indicates the satisfactory performance area, which is defined by the assigned value $\pm 2\sigma_P$ along the x-axis and by the

Figure 1: Graphical presentation of z-scores corresponding to the "values for proficiency assessment" reported by the **NRLs** for the contents of BAA, BAP, BBF, CHR, and the SUM parameter in the spiked olive oil test material.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the last two performance categories.

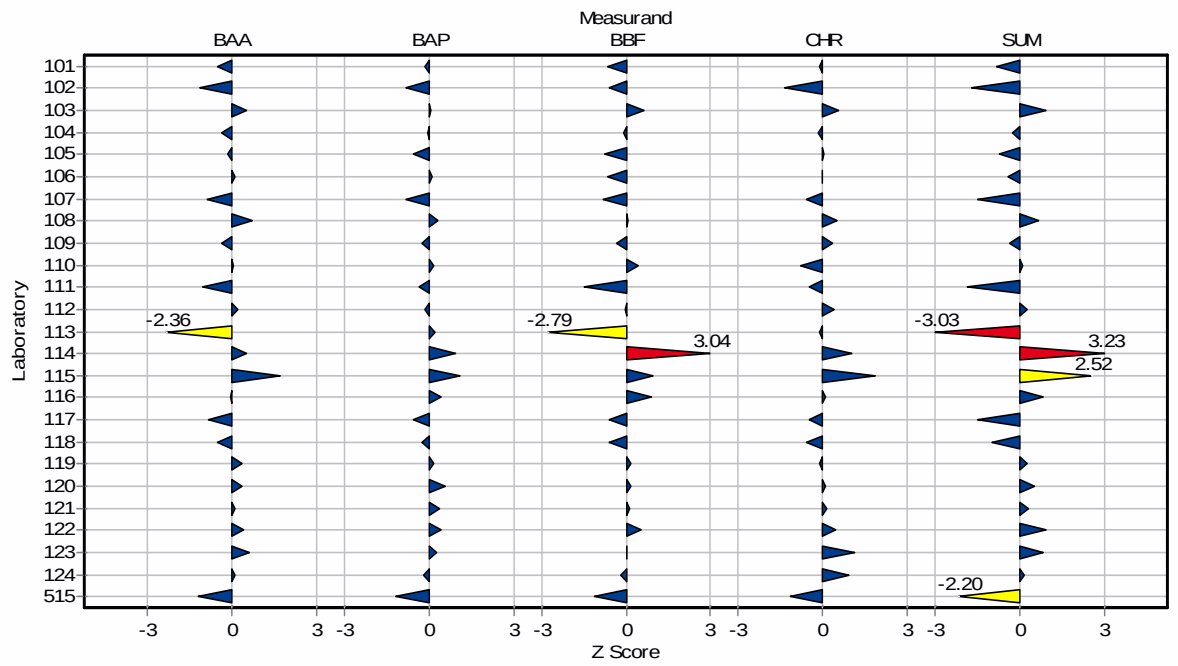


Figure 2: Graphical presentation of z-scores corresponding to the "values for proficiency assessment" reported by the **OCLs** for the contents of BAA, BAP, BBF, CHR, and the SUM in the spiked olive oil test material.

Blue triangles indicate satisfactory performance; yellow triangles indicate questionable performance; red triangles indicate non-satisfactory performance; z-score values are presented above the triangles for the latter performance category.

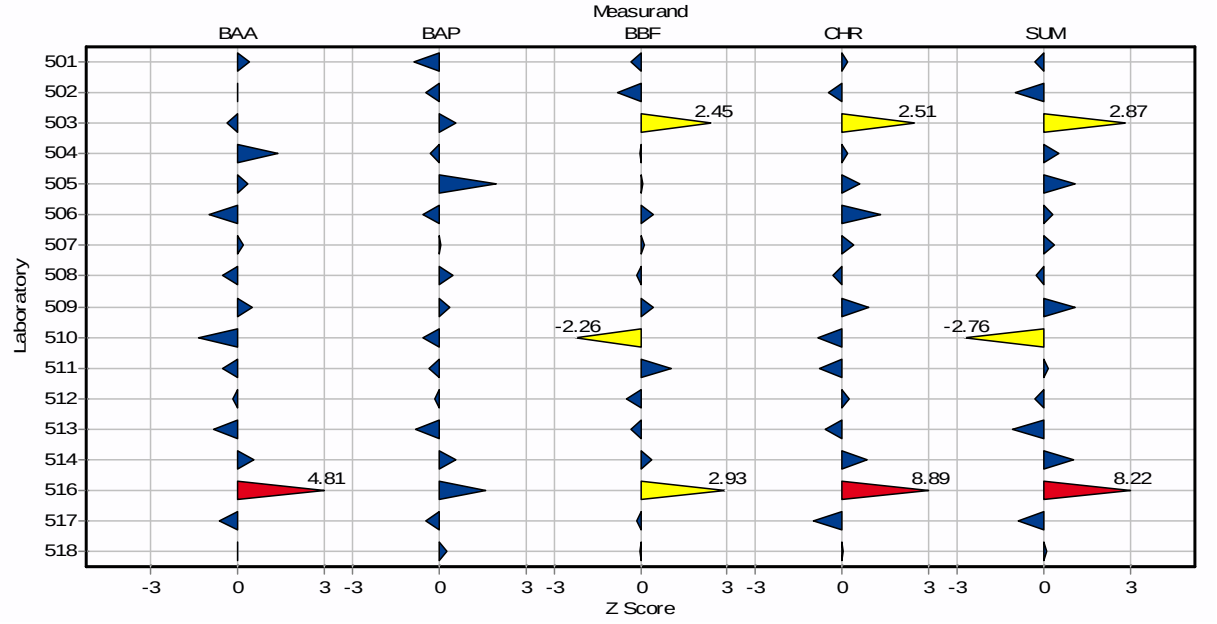


Table 5: Compilation of z-scores calculated from the "results for proficiency assessment" reported by the NRLs and OCLs for test material OIL: z-scores outside the satisfactory range (|z| > 2) are highlighted in red.

	BAA		BAP		BBF		CHR		SUM	
Assigned value, µg/kg	2,79		2,27		5,32		2,77		13,15	
σp, µg/kg	0,58		0,48		1,07		0,57		1,43	
	Result	z-score	Result	z-score	Result	z-score	Result	z-score	Result	z-score
Lab code	µg/kg		µg/kg		µg/kg		µg/kg		µg/kg	
	National Reference Laboratories (NRLs)									
101	2,5	-0,5	2,2	-0,1	4,6	-0,7	2,7	-0,1	12	-0,8
102	2,14	-1,1	1,88	-0,8	4,707	-0,6	1,989	-1,4	10,716	-1,7
103	3,1	0,5	2,3	0,1	6	0,6	3,1	0,6	14,5	0,9
104	2,58	-0,4	2,25	0,0	5,25	-0,1	2,67	-0,2	12,75	-0,3
105	2,7	-0,2	2	-0,6	4,5	-0,8	2,8	0,1	12,1	-0,7
106	2,84	0,1	2,32	0,1	4,65	-0,6	2,76	0,0	12,57	-0,4
107	2,27	-0,9	1,87	-0,8	4,44	-0,8	2,45	-0,6	11,03	-1,5
108	3,21	0,7	2,42	0,3	5,43	0,1	3,05	0,5	14,1	0,7
109	2,58	-0,4	2,14	-0,3	4,95	-0,3	2,98	0,4	12,65	-0,3
110	2,83	0,1	2,36	0,2	5,79	0,4	2,31	-0,8	13,3	0,1
111	2,18	-1,1	2,1	-0,4	3,72	-1,5	2,51	-0,5	10,5	-1,9
112	2,9	0,2	2,2	-0,1	5,3	0,0	3	0,4	13,5	0,2
113	1,42	-2,4	2,37	0,2	2,33	-2,8	2,7	-0,1	8,82	-3,0
114	3,1	0,5	2,73	1,0	8,57	3,0	3,37	1,1	17,77	3,2
115	3,79	1,7	2,81	1,1	6,33	0,9	3,83	1,9	16,76	2,5
116	2,76	-0,1	2,47	0,4	6,28	0,9	2,83	0,1	14,34	0,8
117	2,3	-0,8	2	-0,6	4,7	-0,6	2,5	-0,5	11	-1,5
118	2,5	-0,5	2,14	-0,3	4,66	-0,6	2,44	-0,6	11,73	-1,0
119	3,01	0,4	2,34	0,1	5,49	0,2	2,69	-0,1	13,53	0,3
120	3,01	0,4	2,54	0,6	5,5	0,2	2,81	0,1	13,86	0,5
121	2,85	0,1	2,45	0,4	5,44	0,1	2,86	0,2	13,6	0,3
122	3,03	0,4	2,48	0,4	5,93	0,6	3,04	0,5	14,48	0,9
123	3,14	0,6	2,41	0,3	5,35	0,0	3,42	1,1	14,33	0,8
124	2,84	0,1	2,17	-0,2	5,13	-0,2	3,3	0,9	13,4	0,2
515	2,1	-1,2	1,7	-1,2	4,1	-1,1	2,1	-1,2	10	-2,2
	Official control laboratories (OCLs)									
501	3,037	0,4	1,85	-0,9	4,967	-0,3	2,873	0,2	12,727	-0,3
502	2,781	0,0	2,048	-0,5	4,438	-0,8	2,496	-0,5	11,763	-1,0
503	2,57	-0,4	2,54	0,6	7,94	2,4	4,2	2,5	17,25	2,9
504	3,6	1,4	2,12	-0,3	5,29	0,0	2,89	0,2	13,89	0,5
505	3,01	0,4	3,23	2,0	5,4	0,1	3,11	0,6	14,72	1,1
506	2,21	-1,0	1,99	-0,6	5,77	0,4	3,54	1,4	13,62	0,3
507	2,9	0,2	2,31	0,1	5,47	0,1	3,01	0,4	13,69	0,4
508	2,5	-0,5	2,5	0,5	5,2	-0,1	2,6	-0,3	12,8	-0,2
509	3,1	0,5	2,46	0,4	5,8	0,4	3,3	0,9	14,7	1,1
510	2	-1,4	2	-0,6	2,9	-2,3	2,3	-0,8	9,2	-2,8
511	2,5	-0,5	2,11	-0,3	6,47	1,1	2,31	-0,8	13,39	0,2
512	2,7	-0,2	2,2	-0,1	4,8	-0,5	2,9	0,2	12,7	-0,3
513	2,32	-0,8	1,87	-0,8	4,94	-0,4	2,44	-0,6	11,57	-1,1
514	3,13	0,6	2,55	0,6	5,72	0,4	3,26	0,9	14,66	1,1
516	5,58	4,8	3,04	1,6	8,45	2,9	7,84	8,9	24,91	8,2
517	2,44	-0,6	2,06	-0,4	5,2	-0,1	2,21	-1,0	11,9	-0,9
518	2,8	0,0	2,4	0,3	5,3	0,0	2,8	0,1	13,3	0,1

Table 6: Compilation of zeta-scores calculated from the "results for proficiency assessment" reported by the NRLs and OCLs for test material OIL, the combined reported standard measurement uncertainty, and the uncertainty of the analyte content of the test material:

zeta-Scores outside the satisfactory range (|zeta| > 2) are highlighted in red. Yellow highlighted cells indicate measurement uncertainty values that either did not comply with the thresholds given by the "fitness-for-purpose" function U_f (BAA, BAP, BBF, and CHR), or were not in agreement with the uncertainty value derived from the uncertainties of the individual analytes (SUM parameter).

	BAA			BAP			BBF			CHR			SUM		
Assigned value +/- U, µg/kg	2,79	±	0,02	2,27	±	0,03	5,32	±	0,05	2,77	±	0,03	13,15	±	0,07
σp, µg/kg	0,58			0,48			1,07			0,57			1,43		
	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score	Result	U	zeta-score
Lab code	µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg		µg/kg	µg/kg	
	National Reference Laboratories (NRLs)														
101	2,5	0,49	-1,2	2,2	0,44	-0,3	4,6	0,92	-1,6	2,7	0,54	-0,3	12	1,3	-1,8
102	2,14	0,719	-1,8	1,88	0,523	-1,5	4,707	1,214	-1,0	1,989	0,551	-2,8	10,716	3,007	-1,6
103	3,1	0,6	1,0	2,3	0,5	0,1	6	1,2	1,1	3,1	0,7	0,9	14,5	1,6	1,7
104	2,58	0,67	-0,6	2,25	0,77	-0,1	5,25	1,57	-0,1	2,67	0,59	-0,3	12,75	1,97	-0,4
105	2,7	0,54	-0,3	2	0,4	-1,3	4,5	0,9	-1,8	2,8	0,56	0,1	12,1	1,2	-1,7
106	2,84	0,48	0,2	2,32	0,35	0,3	4,65	0,65	-2,1	2,76	0,44	0,0	12,57	2,14	-0,5
107	2,27	0,31	-3,3	1,87	0,25	-3,2	4,44	0,5	-3,5	2,45	0,72	-0,9	11,03	0,96	-4,4
108	3,21	0,72	1,2	2,42	0,45	0,7	5,43	0,9	0,2	3,05	0,84	0,7	14,1	2,83	0,7
109	2,58	0,45	-0,9	2,14	0,43	-0,6	4,95	1,03	-0,7	2,98	0,52	0,8	12,65	4,82	-0,2
110	2,83	0,58	0,1	2,36	0,48	0,4	5,79	1,17	0,8	2,31	0,49	-1,9	13,3	1,47	0,2
111	2,18	0,14	-8,6	2,1	0,14	-2,4	3,72	0,62	-5,1	2,51	0,47	-1,1	10,5	0,8	-6,6
112	2,9	0,6	0,4	2,2	0,5	-0,3	5,3	1,7	0,0	3	0,5	0,9	13,5	1,9	0,4
113	1,42	0,2	-13,6	2,37	0,38	0,5	2,33	0,35	-16,9	2,7	0,45	-0,3	8,82	0,71	-12,1
114	3,1	0,99	0,6	2,73	0,66	1,4	8,57	1,2	5,4	3,37	0,71	1,7	17,77	1,83	5,0
115	3,79	0,38	5,3	2,81	0,28	3,8	6,33	0,63	3,2	3,83	0,38	5,6	16,76	0,88	8,2
116	2,76	0,7	-0,1	2,47	0,6	0,7	6,28	1,6	1,2	2,83	0,7	0,2	14,34	3,6	0,7
117	2,3	0,69	-1,4	2	0,6	-0,9	4,7	1,41	-0,9	2,5	0,75	-0,7	11	6,6	-0,7
118	2,5	0,28	-2,1	2,14	0,35	-0,7	4,66	0,68	-1,9	2,44	0,28	-2,3	11,73	2,06	-1,4
119	3,01	0,45	1,0	2,34	0,3	0,5	5,49	0,88	0,4	2,69	0,38	-0,4	13,53	3,94	0,2
120	3,01	0,23	1,9	2,54	0,2	2,7	5,5	0,52	0,7	2,81	0,3	0,3	13,86	0,67	2,1
121	2,85	0,43	0,3	2,45	0,24	1,5	5,44	0,82	0,3	2,86	0,36	0,5	13,6	1,02	0,9
122	3,03	0,48	1,0	2,48	0,44	1,0	5,93	1,02	1,2	3,04	0,5	1,1	14,48	1,31	2,0
123	3,14	0,202	3,4	2,41	0,173	1,6	5,35	0,056	0,8	3,42	0,075	16,1	14,33	0,282	8,1
124	2,84	0,1	1,0	2,17	0,2	-1,0	5,13	0,4	-0,9	3,3	0,2	5,2	13,4	1,3	0,4
515	2,1	0,9	-1,5	1,7	0,7	-1,6	4,1	1,7	-1,4	2,1	0,9	-1,5	10	4,2	-1,5
	Official Control Laboratories (OCLs)														
501	3,037	n.r.		1,85	n.r.		4,967	n.r.		2,873	n.r.		12,727	n.r.	
502	2,781	0,5562	0,0	2,048	0,4096	-1,1	4,438	0,8876	-2,0	2,496	0,4992	-1,1	11,763	2,3526	-1,2
503	2,57	0,9	-0,5	2,54	0,89	0,6	7,94	2,78	1,9	4,2	1,47	1,9	17,25	3,39	2,4
504	3,6	0,54	3,0	2,12	0,32	-0,9	5,29	0,79	-0,1	2,89	0,43	0,6	13,89	2,08	0,7
505	3,01	0,78	0,6	3,23	0,84	2,3	5,4	1,43	0,1	3,11	0,81	0,8	14,72	2	1,6
506	2,21	0,63	-1,8	1,99	0,6	-0,9	5,77	1,24	0,7	3,54	0,84	1,8	13,62	1,73	0,5
507	2,9	0,6	0,4	2,31	0,5	0,2	5,47	1	0,3	3,01	0,6	0,8	13,69	3	0,4
508	2,5	0,5	-1,2	2,5	0,375	1,2	5,2	15	-0,3	2,6	0,52	-0,7	12,8	2,56	-0,3
509	3,1	0,6	1,0	2,46	0,49	0,8	5,8	1,2	0,8	3,3	0,7	1,5	14,7	2,9	1,1
510	2	0,8	-2,0	2	0,9	-0,6	2,9	1	-4,8	2,3	0,9	-1,0	9,2	3,6	-2,2
511	2,5	0,64	-0,9	2,11	0,53	-0,6	6,47	1,64	1,4	2,31	0,59	-1,6	13,39	1,93	0,2
512	2,7	0,6	-0,3	2,2	0,7	-0,2	4,8	1	-1,0	2,9	0,6	0,4	12,7	1,5	-0,6
513	2,32	0,28	-3,3	1,87	0,36	-2,2	4,94	0,59	-1,3	2,44	0,46	-1,4	11,57	2,2	-1,4
514	3,13	0,66	1,0	2,55	0,51	1,1	5,72	1,2	0,7	3,26	0,65	1,5	14,66	1,6	1,9
516	5,58	n.r.		3,04	n.r.		8,45	n.r.		7,84	n.r.		24,91	n.r.	
517	2,44	0,52	-1,3	2,06	0,42	-1,0	5,2	1	-0,2	2,21	0,47	-2,4	11,9	2,5	-1,0
518	2,8	0,4	0,0	2,4	0,2	1,3	5,3	1,7	0,0	2,8	0,3	0,2	13,3	n.r.	6,3

n.r.: not reported

average repeatability standard deviation of the results reported by the participants along the y-axis. The latter was obtained by analysis-of-variance of the data set received for each analyte.

Participants whose data are outside the satisfactory performance area should perform root cause analysis. It would be very much appreciated if they would report back to the EU-RL PAH the identified reason for the deviations.

9.4 Additional information extracted from the questionnaire

Additional information was gathered from the questionnaire filled in by the participants (ANNEX 7). Data is presented as reported.

Regarding the experience of the laboratories with this kind of analysis 38 laboratories reported experience of more then one year, 1 laboratory - less then one year and 2 laboratories didn't respond. The distribution in terms of years experience and number of analysis per year between NRLs and OCLs is shown in Figure 3 and 4.

Eighty four percents of the NRLs and 81 percents of OCLs are accredited for the methods of analysis used in this exercise (Figure 5).

More than half of the participants (NRLs and OCLs) used GC/MS (GC/MSMS or HRMS) techniques for performing analysis, while 31% of NRLs and 40% of OCLs applied HPLC/FLD (Figure 6). The analysis of all data revealed that laboratory performance was not linked to any analytical technique or sample preparation method used.

Figure 3. Experience of NRLs (a) and OCLs (b) in years in the analysis of PAH in edible oil

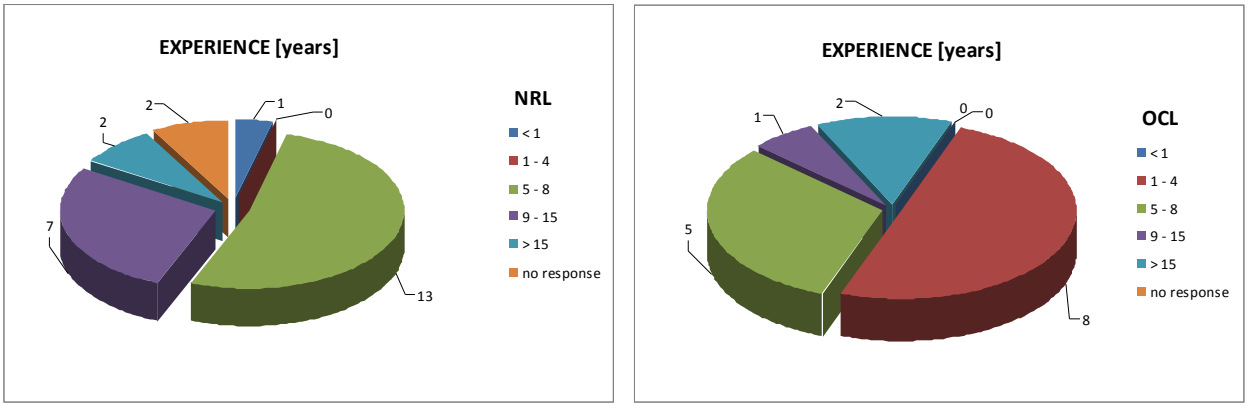


Figure 4. Experience of NRLs (a) and OCLs (b) in the analysis of PAH in edible oil expressed as number of analysis per years

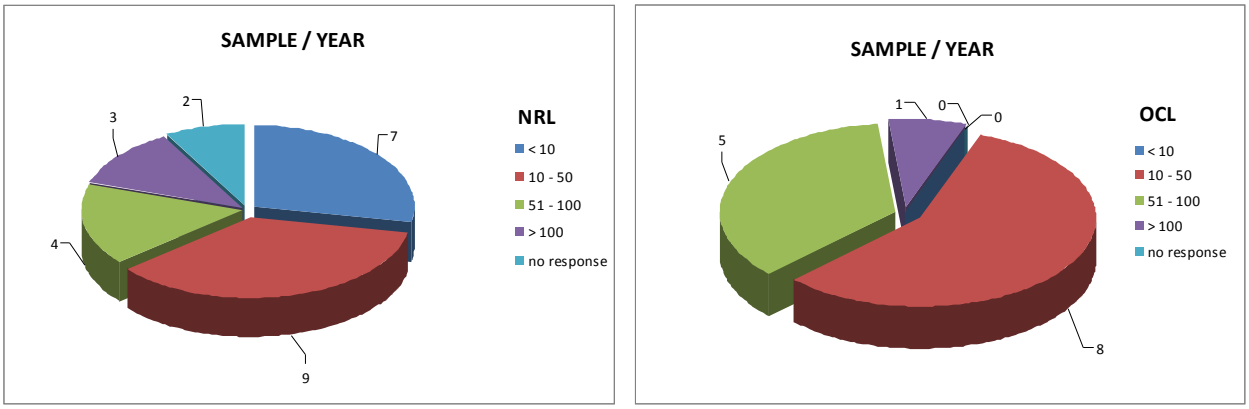
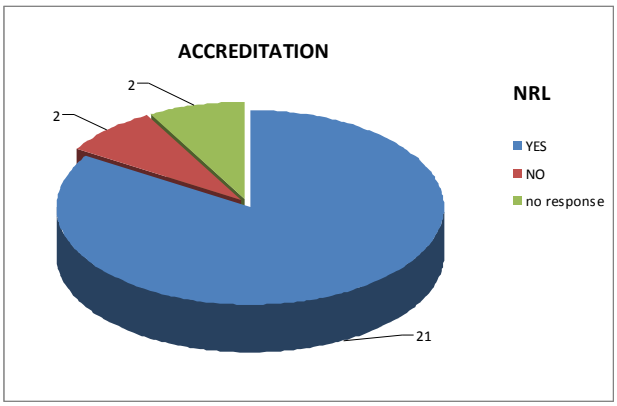


Figure 5. Accreditation of NRLs (a) and OCLs (b) for the methods of analysis used in this PT



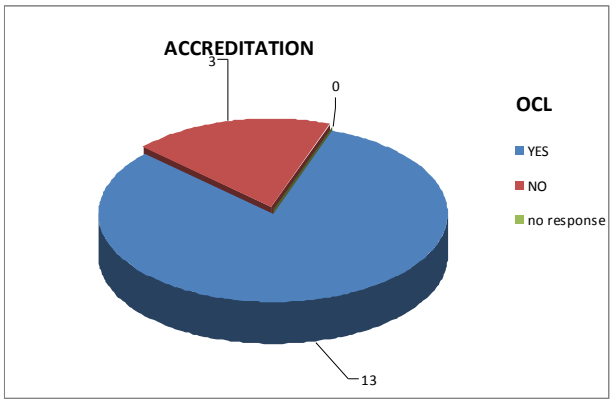
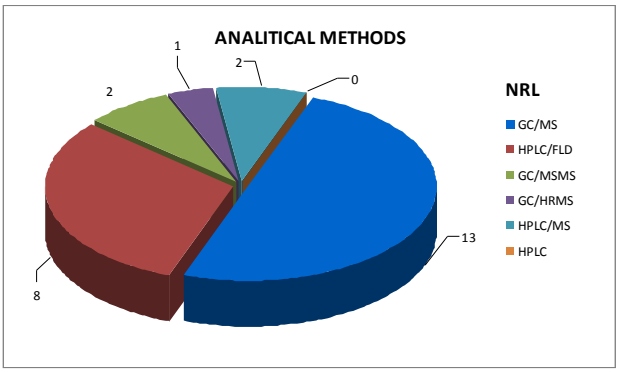
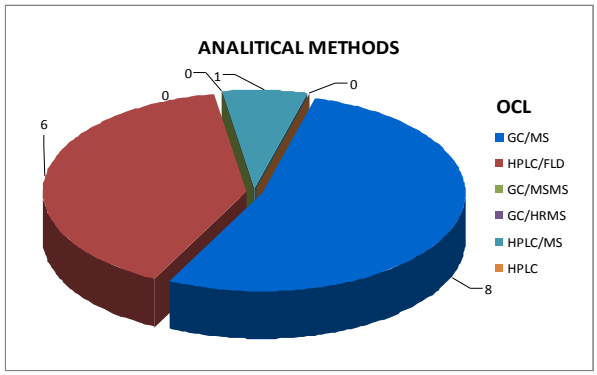


Figure 6. Application of different instrumental methods for determination of PAH in edible oil.





Finally, ANNEX 7 summarises the comments of the participants regarding the organised interlaboratory comparison.

10. Follow-up actions for underperforming laboratories

All NRL laboratories that got "questionable" or "non-satisfactory" performance ratings are urged to perform root cause analysis, and to implement corrective actions.

The EU-RL will set up follow-up measures in due time for all NRLs that received for at least one of the four PAHs (BAA, BAP, BBF, and CHR) z-scores > |3| as required by Regulation (EC) 882/2004, and by the Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with European Union reference laboratories (EU-RLs) activities. These laboratories shall perform as an immediate action root-cause-analysis, and shall report to the EU-RL PAH in writing the identified cause for their underperformance and corrective actions they are going to take. Additionally, they shall participate to an independent (non-EU-RL) proficiency test on the determination of PAHs in food and shall communicate the outcome of this exercise to the EU-RL PAH.

11. Conclusions

Forty-two participants reported analysis results. The performance of most participants was good. In total 94.4 and 90.5 of the results reported by NRLs and OCLs respectively obtained a satisfactory z-score. zeta-Scores were calculated besides z-scores. They indicate the agreement of the reported result with the assigned value with respect to the stated measurement uncertainty. The outcome of this rating was worse than for the z-scores, which reveals that the measurement uncertainty estimates were in some cases not realistic.

12. Acknowledgements

The organizers would like to thank Beatriz de la Calle and Franz Ulberth (all from IRMM, Geel, Belgium) for their accurate revision of this report and all NRLs and OCLs for their cooperation.

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14. ANNEXES

ANNEX 1 – Announcement of the PT on the IRMM webpage

ANNEX 2 – Announcement via e-mail and invitation

ANNEX 3 – Announcement of material dispatch

ANNEX 4 – Documents sent to participants

ANNEX 5 – Technical specifications of the calibration solutions

ANNEX 6 – Homogeneity of the test material

ANNEX 7 – Questionnaire

ANNEX 8 – Data reported by participants

ANNEX 9 - Laboratory means and repeatability standard deviation

ANNEX 1: Announcement of the PT on the IRMM webpage

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EU-RL PT 824: Edible oil

Proficiency Test on the determination of 4 marker PAHs in edible oil

The European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons organises a proficiency test on the determination of 4 marker PAHs (see Table 1) in olive oil.

The objective of this study is to evaluate the capabilities of European National Reference Laboratories (NRLs) and Official Food Control Laboratories (OCLs) in the determination of the target analytes and their sum in edible oil in view of forthcoming legislative updates on maximum levels of PAHs in food.

Only NRLs for PAHs and OCLs as indicated by NRLs can participate in the study.

Participation is admitted to maximum 80 official food control laboratories, which will be accepted in the order of registration.

Participation is free of charge for NRLs for PAHs.

The participation fee is **EUR 250** (two hundred fifty) per registration for OCLs, which do not have NRL status.

Test material and analytes

The test material is a commercial olive oil containing the target analytes (see Table 1). Participants will receive one amber glass ampoule containing about 20g of the spiked olive oil. In addition, participants will get an ampoule with a solution of PAHs with disclosed analyte content, in, depending on their preference, either acetonitrile or toluene. This solution will be supplied to allow the participants verifying their instrument calibration against an independent standard.

Table 1: The target analytes of the comparison

benz[a]anthracene (BaA)
benzo[b]fluoranthene (BbF)
benzo[a]pyrene (BaP)
chrysene (CHR)
Sum of the four marker PAHs

General outline

Participants are requested to perform three independent analyses of the edible oil. These analyses shall be performed on the same day. Participants have to report the results for individual analytes of the replicate analyses. These results have to be reported corrected for recovery.

Participants will be also asked to report a single value for scoring, the "final value", both for the individual analytes as well as for the sum of the four marker PAHs. These results will have to be reported corrected for recovery and have to be accompanied by the respective measurement uncertainty.

Further details will be communicated to participants at a later stage.

Performance assessment:

The performance of the participants in the determination of PAHs in olive oil will be rated by Z-scores and zeta-scores.

The standard deviations for proficiency assessment will be derived:

- For the four individual target analytes, from the fitness-for-purpose function given in Commission Regulation (EC) No 333/2007, assuming a value of 0.3 µg/kg for the limit of detection.
- For their sum, the target standard deviations will be obtained from the truncated Horwitz equation (-sigma- =22% C, where C is the assigned value)

Registration

Registration shall be done via https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=824

Schedule

Registration deadline	Sample dispatch	Reporting of results	Report
12 october 2012	Second half of October 2012	6 weeks from sample dispatch	February 2013

Contacts

Jrc-irmm-crl-pah@ec.europa.eu

ANNEX 2: Announcement of the PT via invitation

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
European Union - Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 28/09/2012
JRC.D.5/TW/bk/ARES(2012)1140882

Interlaboratory comparison of the EU-RL for Polycyclic Aromatic Hydrocarbons (PAHs) in olive oil

Dear Madame/Sir,

Registration for participation in the inter-laboratory comparison study organised by the EU-RL PAH on the determination of the 4 marker PAHs in olive oil will be **open from 28 September to 12 October 2012**.
Participation is mandatory and free of charge for National Reference Laboratories (NRLs) for PAHs. Confidentiality of participants and respective results is granted.

In support to the NRLs, to facilitate fulfilling their tasks as included in Regulation (EC) No 882/2004, EU Official Food Control Laboratories (OCLs) falling under the responsibility of the NRLs may participate in the study. **The participation fee for official food control laboratories is 250 Euro per participation.**

The target analytes are listed in the following Table.

benz[*a*]anthracene (BaA)
benzo[*b*]fluoranthene (BbF)
benzo[*a*]pyrene (BaP)
chrysene (CHR)
SUM of the 4 marker PAHs

Results have to be reported corrected for recovery and accompanied by the respective measurement uncertainty for both the individual PAHs and the sum of the four marker PAHs.

Each participant will be provided with one amber glass ampoule containing ~ 20 g of olive oil.
Participants will also receive a standard solution in either acetonitrile or toluene with disclosed content; which might be used for verification of instrument calibration.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-crl-pah@ec.europa.eu

Detailed information will be soon available the EU-RL website:
http://irmm.jrc.ec.europa.eu/EURLs/EURL_PAHs/interlaboratory_comparisons/Pages/index.aspx

Timing:

- **Deadline for registration: 12 October 2012**
- Dispatch of samples: second half of October 2012. A detailed outline of the study will be included in the parcels. Participants will be asked to return a sample receipt to the organiser
- Deadline for reporting of results: six weeks from dispatch of samples. You will receive the link for entering the results upon reception of the PT samples

Registration procedure:
Participants shall register via this link:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=824

In order to register, laboratories must:

1. **Enter** the details on line:
2. **Print** the completed form (approved and confirmed version) when the system asks to do so, sign it and stamp it with your company stamp
3. **Send** it to the EU-RL PAHs members indicated below, either via FAX or via e-mail

PT coordinator	Second contact
Thomaz Wenzl	Stefanka Bratinova
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

Participants will be requested to indicate the preferred solvent type of the standard solutions (either toluene or acetonitrile) prior to dispatch of samples via a separate email.

Distribution of information:
The NRLs are kindly requested to distribute as soon as possible this information to the OCLs under their responsibility, and to assist the EU-RL in identifying laboratories that are eligible to participate in the study.

Access of NRLs to performance data of official food control laboratories:
Two options:

1) *NRL enrols OCLs and covers participation fee.*
NRL submits to EU-RL list of participants including name and address of laboratory, and details of the contact person (name, address - no post box! - email and telephone number). The coverage of the participation fees has to be

confirmed and details for invoicing (e.g. order number) have to be provided. It shall be made clear, that the full participation fee is payable upon dispatch of the test samples. In return, the performance data of the respective official food control laboratories will be disclosed to the NRL.

2) The *OCL (identified as such by the respective NRL) enrols itself* in the inter-laboratory comparison *and covers the participation fee.*
The NRL will get access to performance data of the OCL only upon providing to the EU-RL for PAHs a letter of consent.

In case you may wish clarification of open questions, please do not hesitate to contact the EU-RL team via:

JRC-IRMM-CRL-PAH@ec.europa.eu

With kind regards,

Stefanka Bratinova

On behalf of

Thomas Wenzl
(Operating Manager of the EU-RL PAHs)

Cc: Thomas Wenzl, Beatriz de la Calle, Franz Ulberth

ANNEX 3: Announcement of material dispatch

From: VERLINDE Philippe (JRC-GEEL) on behalf of JRC IRMM CRL PAH Sent: Wed 07/11/2012 11:12

To: JRC IRMM CRL PAH

Cc: BITTERHOF Almut (SANCO)

Bcc: 'germuska@svpudk.sk'; 'honzlova@svujihlava.cz'; 'ilona.honga@terviseamet.ee'; 'joe.holland@fera.gsi.gov.uk'; 'mirja.hokkanen@evira.fi'; 'rudolf.hackenberg@bvl.bund.de'; 'ijarmalaite@vet.lt'; 'KusnyarikE@nebih.gov.hu'; 'peeter.laumann@terviseamet.ee'; 'snezana.lobnik@zzv-mb.si'; 'macak@svu-ke.sk'; 'martingmj@madrid.es'; 'dno@nifes.no'; 'jan.rosmus@svupraha.cz'; 'ruiz_lou@gva.es'; 'astarski@pzh.gov.pl'; 'claude.schummer@lns.etat.lu'; 'jean-pierre.sageder@ages.at';

Subject: Proficiency test on the determination of PAHs in olive oil (PT 824)

Dear Madame/Sir,

The test samples for the proficiency test on the determination of four EU marker PAHs in olive oil (PT 824) are dispatched today.
You should expect receipt of the parcel within 72 hours at the latest.

Please check the completeness of the delivery and confirm it by filling and retourning the sample receipt form to us (by fax) You will find the form in an envelop in the parcel together with your participation key, the outline of the study, the reporting instructions and the specification of the standard solution.

Please contact us in case you do not receive the samples by end of this week.

Deadline for reporting of analysis results is 4 January 2013.

With best regards

Philippe Verlinde

European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons (EU-RL PAH)

European Commission
DG Joint Research Centre (JRC)
Unit D.5 Food Safety and Quality (FSQ)

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philippe.verlinde@ec.europa.eu
http://www.jrc.ec.europa.eu <http://www.jrc.ec.europa.eu>

ANNEX 4: Documents sent to participants - OUTLINE

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

EURL
European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 25/10/2012

ILC-824

Eleventh Inter-laboratory comparison study organised by the EU-RL PAHs

Analysis of the four marker PAHs in olive oil

General description

The test material is olive oil. Target analytes are the four marker PAHs (listed in Table 1). Additionally laboratories have to report their sum.

The EU-RL PAHs will check for the four target analytes the compliance of the performed analyses with provisions given in Regulation (EU) No 836/2011.

Participating laboratories will be scored for each of the four PAHs, plus for their sum.

Table 1: The target analytes of the comparison (four marker PAHs)

benz[*a*]anthracene (BaA)
benzo[*b*]fluoranthene (BbF)
benzo[*a*]pyrene (BaP)
chrysene (CHR)
SUM of the 4 marker PAHs

The content of the parcel

Each participant will be provided with a set of samples that comprises:

- One ampoule, labelled as "OIL-2012 - XXX", containing about 20 g of spiked olive oil. The concentration of the individual analytes is in the range from about 0 to 10 µg/kg. This sample **is the test sample of the PT**.
- One ampoule, labelled as "ACN-10/2012-K/XXX" or as "TOL-10/2012-K/XXX" depending on the solvent you chose, acetonitrile or toluene respectively, containing about 1 ml of a solution of the *four marker PAHs in solvent (acetonitrile or toluene)*. The concentration of the individual analytes is reported in the respective specification sheet and is therefore **known to participants**. Please bear in mind that these solutions *do not contain any internal standards*.

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E-mail: jrc-irmm-crhpal@ec.europa.eu

Olive oil samples are to be stored at room temperature and solutions at 4°C in the dark

Participants will also receive:

- the a sample receipt form (to be filled in and sent back to the EU-RL as soon as possible)
- the outline of the study (a printout of this document)
- the participation (password) key (to be used for all following communication concerning this PT)
- specification sheets for the solutions of known content
- material safety data sheets for some of the analytes and for the solvents

Outline of the study

1. The laboratories are requested to perform **three (3) replicate analyses on the contaminated olive oil material.** The sample shall be analysed immediately after opening of the ampoule, and the three replicates should be analysed under repeatability condition. A **"final value", which is the value applied for scoring,** is also required for each analyte beside the results obtained from replicate analysis. In addition, participants are asked to report a value for the sum of the four target PAHs.

2. The **known solution of PAHs in solvent** may be used by participants as an external reference to check their instrument calibration.

For all samples the participating laboratories shall apply a method of their choice, taking into account that other PAHs than the four marker PAHs could be present.

Reporting of the results will be open on 13th November 2012. The laboratories shall report the results by **4th January 2013 at the latest** via the ILC web interface using the participation (password) key, shipped together with the test samples (in the same parcel).

Scoring system

The assigned values will be obtained from the gravimetrical preparation of the materials. They will be verified by chemical analysis.

The target standard deviations will be set:

- for the four individual PAHs as equal to the value derived from the uncertainty function (Uf) according to Commission Regulation (EU) No 836/2011.

- for the sum of the four marker PAHs as equal to the combined standard uncertainty derived from the Uf of the four individual marker PAHs, according to the equation below:

- $Uf(SUM) = \sqrt{U_f^2(BaA) + U_f^2(BaP) + U_f^2(BbF) + U_f^2(CHR)}$

z-scores and zeta(ζ)-scores will be assigned for the marker PAHs (**BaA**, **BaP**, **BbF**, and **CHR)** (see Table 1 for full names) and their sum on the base of the reported final value. For these five measurands a non reported final value (an empty cell in the reporting system) will be considered as underperformance. In case the content was found to be below the LOD, the scoring will be calculated upon the concentration corresponding to the LOD reported.

In case of questions please do not hesitate to contact:

PT coordinator	**Second contact**
Thomas Wenzl	Stefanka Bratinova
Fax: 0032-14-571783 e-mail: jrc-irmm-crl-pah@ec.europa.eu	

With kind regards,

Thomas Wenzl

(Operating Manager of the European Union Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

Cc: Almut Bitterhof, Michael Flueh, Franz Ulberth, Beatriz de la Calle, Stefanka Bratinova

INSTRUCTIONS

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

Geel, 25-10-2012

Reporting instructions

In the parcel participants will find their **password key** and the **participant secret code** as well as **the link for reporting.** The participant secret code will be used in the report for generating Tables and graphics.

The password key is needed to get access to the interface for reporting of results and for filling in the questionnaire. **All characters of the key should be entered as they are** (e.g. keeping capital letters).

Please remember to save frequently your entries so to avoid any loss of data in case of malfunctioning of the server. **The filling in of all fields marked with a * is mandatory**.

As a support for the reporting steps, PDF preview is available for both data reporting and questionnaire.

Each page of the results reporting interface corresponds to a sample as they are listed in Table 2 below (use the arrows on top of the page to move across pages).

Table 2: The samples of the comparison

Page	Sample	Field name in the reporting interface
Page 1	Spiked olive oil replicates	OIL-REP replicate 1/2/3
Page 2	Spiked olive oil final value	OIL-FIN (for proficiency assessment) single value

The reporting page is structured like a table. To facilitate the compilation of results, it is also possible to download an excel template, in which results may be entered offline. This file has to be saved with a different name on the participant's PC, filled in (without modifying its structure!) and uploaded again in the interface.

After you entered the results directly, or via upload from the Excel table, you still have the possibility to modify entries, if deemed necessary. By clicking on the button "Validate and save" the interface verifies that all mandatory data were correctly entered by the participant.

After having validated all the data, by clicking on the button "Cancel" you are sent to the main page and proceed with the questionnaire.

After having completed the questionnaire and validated it, by clicking on the button "Cancel" you are sent to the main page.

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From the main page you can print the PDF of the data entered and decide whether to modify them or to proceed with the **final submission** of your data, by clicking the button "Submit".

You shall then print and sign the final PDF and send it back by fax or by mail to the EU-RL mailbox (jrc-irmm-crl-pah@ec.europa.eu). **Reporting of proficiency test data finishes with sending of the signed printout.**

Reporting of RESULTS

Participants shall report:

- for the olive oil sample the **individual results** obtained by replicate analysis (in the web interface labelled as OIL-REP replicate 1/2/3) for the four individual analytes **BaP, BaA, BbF, and CHR** only. Results have to be reported in **µg/kg and corrected for recovery.** In case the content measured should be below the LOD, then the prefix "<" shall be entered instead of the default sign = in the field before the result and the numeric value of the **LOD, expressed** in µg/kg, shall be entered.

- for the olive oil sample a **"final value",** which is the value which will be used for calculation of performance indicators (OIL-FIN (for proficiency assessment) in the web interface) applying following provisions:
  - the content of the four individual analytes **BaP, BaA, BbF, and CHR**, shall be expressed in **µg/kg.** The results have to be corrected for recovery and accompanied by their uncertainty. In case the content measured should be below the LOD, then the prefix "<" shall be entered instead of the default sign = in the field before the result and the numeric value of the **LOD, expressed** in µg/kg, shall be entered.
  - **the sum of the four marker PAHs**: the sum of the contents of the four marker PAHs shall be expressed in **µg/kg** and corrected for recovery, and has to be accompanied by its uncertainty

IMPORTANT: the choice of the final value (average of the replicates, robust mean of the replicates, etc.) is with the participant. Please note that participants will be scored upon the **final value for the target four marker PAHs and their sum.** Uncertainty has to be reported for the final values only. It has to be reported in µg/kg and should be expressed as **expanded uncertainty with a coverage factor of 2** (it is not necessary to enter the coverage factor k unless it is different from 2).

Questionnaire

Participants will be asked to report together with the results also relevant method performance characteristics, a description of the method and of the possible problems encountered when applying their method to this PT samples, and, additionally, some general information on their laboratory.

For the list of questions, please note that if a question mark is displayed beside the question, you can select it to receive additional information on the question and on what the answer should include. Please also note that all fields marked with a * are mandatory.

Concerning the Table of method performances (*use the acronyms listed in Table 1 for reporting*), please follow the following instructions: • The LOD has to be reported in µg/kg (**IMPORTANT:** check that the LOD entered in this Table is the same as the LOD entered in the results in case the result was entered as < LOD) • The LOQ has to be reported in µg/kg • The lower limit of the working range has to be reported in µg/kg • The higher limit of the working range has to be reported in µg/kg • The recovery has to be reported in %	

SAMPLE RECEIPT

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ILC-824

Eleventh Inter-laboratory comparison study organised by the EU-RL PAHs

Analysis of the four marker PAHs in olive oil

Confirmation of the receipt of the samples: RECEIPT FORM

Surname of Participant	
First name of Participant	
Institute	
Address	
Country	

Content of the parcel

a) One amber glass ampoule containing about 20 g of spiked olive oil
b) One brown glass ampoule with 1 ml standard solution of PAHs in solvent (acetonitrile or toluene) (concentrations known)
c) A specification sheet for the item b) content (standard solution)
d) Material safety data sheets for acetonitrile / toluene
e) One outline of the study and reporting instructions
f) One paper sheet with the Laboratory ID (assigned for anonymous evaluation of data and for the PT report to be kept for all further communication) and the Password key (for accessing the webpage for reporting data)
g) One inter-laboratory comparison sample receipt form (= this form)

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E-mail: jrc-irmm-crl-pah@ec.europa.eu

Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:

Date of the receipt of the test materials	
All items have been received undamaged	YES / NO
If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the numeric code too) Please write one item per row	
Items are missing	YES / NO
If YES, please list missing items according to the letters associated at each item in the list above Please write one item per row	
Serial number of the spiked olive oil sample you received	
Serial number of the standard solution(s) with known concentrations you received	

Signature .....

ATTENTION

Please, submit the filled in form by mail to the following address:

jrc-irmm-crl-pah@ec.europa.eu

or print it and send the printout by fax at the attention of Stefanka Bratinova at the following number:

+32 – 14 - 571783

PARTICIPANT CODES

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements (Geel)
European Union Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

Geel, 09.11.2012

«Title» «Firstname» «Surname»
«Organisation», «Department»
«Address»
«Zip»«Town»
«Country»

Dear Madame/Sir,

Please find below your participation key for ILC 824 PAH in oil 2012.

You need this unique key for the reporting of results via the web portal: http://irmm.jrc.ec.europa.eu/Pages/ilcReporting.aspx

Participation/password key:

«Part_key»

Your laboratory code is:

«LCode»

Results have to be reported before 4 January 2013!

With best regards

Thomas Wenzl

(Operating manager of the EU-RL PAHs)

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ANNEX 5: Technical specifications of the calibration solutions

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Institute for Reference Materials and Measurements
European Union - Reference Laboratory for Polycyclic Aromatic Hydrocarbons

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European Union Reference Laboratory
Polycyclic Aromatic Hydrocarbons

Geel, 19.12.2012

Standard solution specification sheet	**Product ID: ACN-10/2012-K**
Date of production: 24/10/2012	Total volume: 1 mL
Expiry date: *May 2013*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/ml)	U** ± %
1	Benz[*a*]anthracene	56-55-3	64.1	50.0	0.39
2	Benzo[*a*]pyrene	50-32-8	63.6	49.6	0.53
3	Benzo[*b*]fluoranthene	205-99-2	63.8	49.7	0.87
4	Chrysene	218-01-9	63.9	49.8	0.83
5	SUM PAH4		255.3	199.2	1.37

** The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Acetonitrile : Toluene (m:m, 99.4: 0.6)

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European Union - Reference Laboratory for Polycyclic Aromatic Hydrocarbons

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Geel, 19.12.2012

Standard solution specification sheet	**Product ID: TOL-10/2012-K**
Date of production: 24/10/2012	Total volume: 1 mL
Expiry date: *May 2013*	

Standard solution composition:

	Product name	CAS	Conc.* (ng/g)	Conc.* (ng/ml)	U** ± %
1	Benz[*a*]anthracene	56-55-3	58.7	50.8	0.39
2	Benzo[*a*]pyrene	50-32-8	58.3	50.4	0.53
3	Benzo[*b*]fluoranthene	205-99-2	58.4	50.5	0.87
4	Chrysene	218-01-9	58.5	50.6	0.83
5	SUM PAH4		234.0	202.3	1.37

** The concentrations were calculated taking into account the purity statements of the single products. The concentration value given in ng/mL is based on the gravimetrical preparation data and the nominal volume of the applied volumetric flask.*

*** U is the expanded uncertainty calculated by multiplying the combined standard uncertainty with the coverage factor 2 (corresponding to a confidence level of 95%). The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent: Toluene

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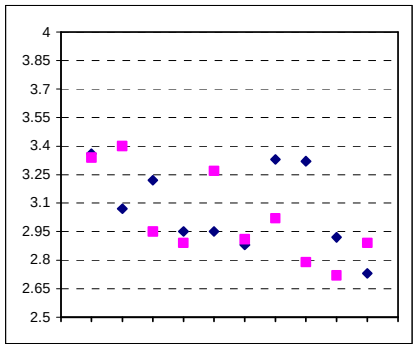
ANNEX 6: Homogeneity of the test material

Analyte: **BAA**

	n =	10		
	mean =	3.0455	21%	**= σ-trg(%)**
0.032880278	**s_x =**	0.1813	0.6414	**= σ-trg**
ÖMSW =	**s_w =**	0.1913		
	s_s =	0.1208	0.1924	**= 0,3*s**

ISO-13528	passed		
F =	0	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	0.0146	0.1066	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	3.36	3.34	0.02	6.7	3.35
Ampoule 026	3.07	3.4	-0.33	6.47	3.235
Ampoule 039	3.22	2.95	0.27	6.17	3.085
Ampoule 077	2.95	2.89	0.06	5.84	2.92
Ampoule 095	2.95	3.27	-0.32	6.22	3.11
Ampoule 102	2.88	2.91	-0.03	5.79	2.895
Ampoule 120	3.33	3.02	0.31	6.35	3.175
Ampoule 159	3.32	2.79	0.53	6.11	3.055
Ampoule 174	2.92	2.72	0.2	5.64	2.82
Ampoule 187	2.73	2.89	-0.16	5.62	2.81



$\sum$**(diff)^2 =** 0.7317

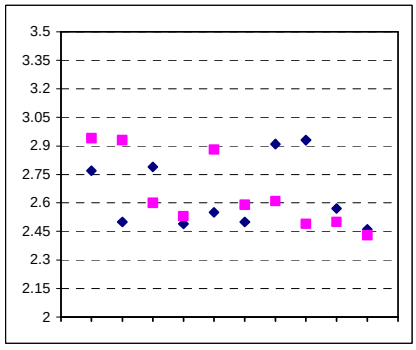
var(sum)/2 = 0.06576 =MSB

Analyte: **BAP**

	n =	10		
	mean =	2.6485	21%	**= σ-trg(%)**
0.017116944	**s_x =**	0.1308	0.5578	**= σ-trg**
ÖMSW =	**s_w =**	0.1814		
	s_s =	0.0259	0.1673	**= 0,3*s**

ISO-13528	passed		
F =	0	3.02038295	= Fcrit
	passed		
IUPAC			
(MSB-MSW)/2	0.0007	0.0859	= F1*(0,3*s)^2+F2*MSW
	passed		

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	2.77	2.94	-0.17	5.71	2.855
Ampoule 026	2.5	2.93	-0.43	5.43	2.715
Ampoule 039	2.79	2.6	0.19	5.39	2.695
Ampoule 077	2.49	2.53	-0.04	5.02	2.51
Ampoule 095	2.55	2.88	-0.33	5.43	2.715
Ampoule 102	2.5	2.59	-0.09	5.09	2.545
Ampoule 120	2.91	2.61	0.3	5.52	2.76
Ampoule 159	2.93	2.49	0.44	5.42	2.71
Ampoule 174	2.57	2.5	0.07	5.07	2.535
Ampoule 187	2.46	2.43	0.03	4.89	2.445



$\sum$**(diff)^2 =** 0.6579

var(sum)/2 = 0.03423 =MSB

Analyte: **BBF**

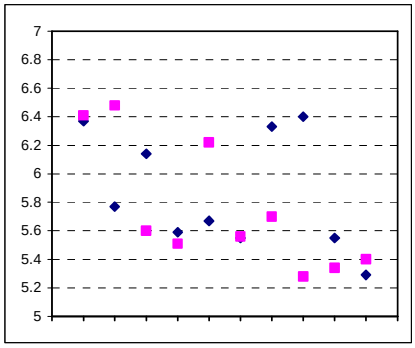
	n =	10		
	mean =	5.8080	20%	= **σ-trg(%)**
0.109156667	s_x =	0.3304	1.1732	= **σ-trg**
ÖMSW =	s_w =	0.3751		
	s_s =	0.1970	0.3520	= **0,3*s**

ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC
(MSB-MSW)/2 0.0388 0.3750 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	6.37	6.41	-0.04	12.78	6.39
Ampoule 026	5.77	6.48	-0.71	12.25	6.125
Ampoule 039	6.14	5.6	0.54	11.74	5.87
Ampoule 077	5.59	5.51	0.08	11.1	5.55
Ampoule 095	5.67	6.22	-0.55	11.89	5.945
Ampoule 102	5.55	5.56	-0.01	11.11	5.555
Ampoule 120	6.33	5.7	0.63	12.03	6.015
Ampoule 159	6.4	5.28	1.12	11.68	5.84
Ampoule 174	5.55	5.34	0.21	10.89	5.445
Ampoule 187	5.29	5.4	-0.11	10.69	5.345



∑**(diff)**^{2} = 2.8138
var(sum)/2 = 0.21831 =MSB

Analyte: **CHR**

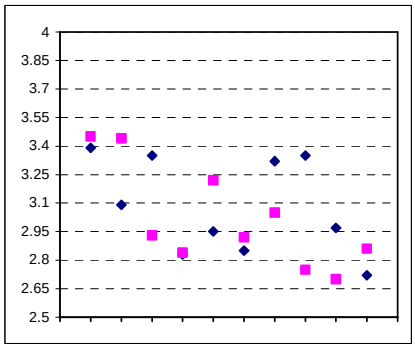
	n =	10		
	mean =	3.0490	21%	= **σ-trg(%)**
0.044215556	s_x =	0.2103	0.6318	= **σ-trg**
ÖMSW =	s_w =	0.2128		
	s_s =	0.1469	0.1895	= **0,3*s**

ISO-13528 passed

F = 0 3.02038295 = Fcrit
passed

IUPAC
(MSB-MSW)/2 0.0216 0.1133 = F1*(0,3*s)^2+F2*MSW
passed

Bottle	Result a	Result b	diff	sum	avg
Ampoule 020	3.39	3.45	-0.06	6.84	3.42
Ampoule 026	3.09	3.44	-0.35	6.53	3.265
Ampoule 039	3.35	2.93	0.42	6.28	3.14
Ampoule 077	2.83	2.84	-0.01	5.67	2.835
Ampoule 095	2.95	3.22	-0.27	6.17	3.085
Ampoule 102	2.85	2.92	-0.07	5.77	2.885
Ampoule 120	3.32	3.05	0.27	6.37	3.185
Ampoule 159	3.35	2.75	0.6	6.1	3.05
Ampoule 174	2.97	2.7	0.27	5.67	2.835
Ampoule 187	2.72	2.86	-0.14	5.58	2.79



∑**(diff)**^{2} = 0.9058
var(sum)/2 = 0.08843 =MSB

ANNEX 7: Questionnaire

BLANK TEMPLATE

1. **Did you find the instructions distributed for this PT adequate?** *
- ◯ a) Yes
- ◯ b) No

1.1. If NO, please report about possible lacking information *

2. **Did you experience any specific problem related to the organisation of this PT?**
- ◯ a) yes
- ◯ b) no

2.1. If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc) *

3. **Did your laboratory quantify PAHs in EDIBLE OIL before?** *
- ◯ a) yes
- ◯ b) no

3.1. If YES, for how long? (expressed in years) *
- ◯ a) <1
- ◯ b) 1-4
- ◯ c) 4-8
- ◯ d) 8-15
- ◯ e) >15
- ◯ f) other

3.1.1. If OTHER, please specify *

3.2. If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? *
- ◯ a) < 10
- ◯ b) 10-50
- ◯ c) 50-100
- ◯ d) > 100
- ◯ e) other

- Page 3 of 6 -

3.2.1. If OTHER, please specify *

4. **Is your laboratory accredited for the determination of PAHs in food?** *
- ◯ a) yes
- ◯ b) no

4.1. If YES, please specify the food matrix included in the accreditation scope *
- ◯ a) Oils and fats (6.1.1)
- ◯ b) Smoked meats and smoked meat products (6.1.2)
- ◯ c) Muscle meat of smoked fish and smoked fishery products (6.1.3)
- ◯ d) Muscle meat of fish (6.1.4)
- ◯ e) Crustaceans, cephalopods, other than smoked (6.1.5)
- ◯ f) Bivalve molluscs (6.1.6)
- ◯ g) Processed cereal-based foods and baby foods for infants and young (6.1.7)
- ◯ h) Infant formulae and follow-on formulae (6.1.8)
- ◯ i) Dietary foods for special medical purposes (6.1.9)
- ◯ j) OTHER
- ◯ k) All the matrices listed above
- ◯ l) the following of the matrices listed above

4.1.1. If OTHER, please specify *

4.1.2. If you chose "the following of the matrices listed above", please report the corresponding codes *

4.2. If YES, please specify the PAHs included in the accreditation scope *
- ◯ a) BaP
- ◯ b) 4 marker PAHs
- ◯ c) 15+1 EU priority PAHs
- ◯ d) 16 EPA PAHs
- ◯ e) other

- Page 4 of 6 -

4.2.1. If OTHER, please specify *

5. **How did you prepare the sample?** *

- a) Dilution
- b) No preparation
- c) Other

5.1. If OTHER, please describe *

6. **Which extraction method did you use?** *

- a) Saponification
- b) Pressurized liquid extraction
- c) Soxhlet extraction
- d) No extraction
- e) Other

6.1. If OTHER, please describe *

7. **Which was the MAIN purification step of your method?** *

- a) Donor-Acceptor Complex Chromatography (DACC)
- b) Size-Exclusion Chromatography
- c) Solid Phase Extraction (SPE)
- d) Solvent partitioning
- e) Other

7.1. If OTHER, please describe *

8. **Which was the instrumental detection method you applied?** *

- a) HPLC-FLD
- b) UHPLC-FLD
- c) HPLC-FLD-UV
- d) UHPLC-FLD-UV
- e) HPLC-MS
- f) UHPLC-MS
- g) HPLC-MS/MS
- h) UHPLC-MS/MS
- i) GC-FID
- j) GC-MS
- k) GC-HRMS
- l) GC-MS/MS
- m) Other

8.1. If OTHER, please describe *

9. **In case you applied a gaschromatographic technique, please describe the analytical column used (stationary phase, length, internal diameter, film thickness)**

10. **In case you applied a liquid chromatographic technique, please describe the analytical column used (stationary phase, particle size, length, internal diameter)**

11. **Did you encounter any problems during the analysis of the sample?** *

- a) Yes
- b) No

11.1. If YES, please describe *

12. **In the following field you may add any further information about this PT and the analysis of the samples**

QUESTIONNAIRE:

On the organisation of the PT

- Did you find the instructions distributed for this PT adequate?
- If NO, please report about possible lacking information (for NRLs no matching case)
- Did you experience any specific problem related to the organisation of this PT?
- If YES, please describe here the main problems you were confronted with (e.g. registration, reporting of results, questionnaire, content of the parcel, material quantity/stability/packaging, instructions concerning the samples, etc)
- In the following field you may add any further information about this PT and the analysis of the samples

NRLs

LabID	Instructions adequate	Lacking information	Organisation problems	Organisation problems description	Additional comments
101	a) Yes	b) no	b) no		b) no
102	a) Yes	b) no	b) no		b) no
103	a) Yes	b) no	b) no		b) no
104	a) Yes	b) no	b) no		b) no
105	a) Yes	b) no	b) no		b) no
106	a) Yes	b) no	b) no		b) no
107	a) Yes	b) no	b) no		b) no
108	a) Yes	b) no	b) no		b) no
109	a) Yes	b) no	b) no		b) no
110	a) Yes	b) no	a) yes	The communication of the error happened to late, which caused an extra time consumption.	b) no
111	a) Yes	b) no	b) no		b) no
112	a) Yes	b) no	b) no		b) no
113	a) Yes	b) no	b) no		b) no
114	a) Yes	b) no	b) no		b) no
115	a) Yes	b) no	a) yes	The change of standard solution specification sheet	b) no
116					
117	a) Yes	b) no	b) no		b) no
118	a) Yes	b) no	b) no		b) no
119	a) Yes	b) no	b) no		b) no
120	a) Yes	b) no	b) no		b) no
121	a) Yes	b) no	b) no		b) no
122	a) Yes	b) no	b) no		b) no
123	a) Yes	b) no	b) no		b) no
124					
515	a) Yes	b) no	b) no		b) no

OCLs

LabID	Instructions adequate	Organisation problems	Organisation problems description	Additional comments
501	a) Yes	b) no		b) no
502	a) Yes	b) no		b) no
503	a) Yes	b) no		b) no
504	a) Yes	b) no		b) no
505	a) Yes	b) no		b) no
506	a) Yes	b) no		b) no
507	a) Yes	b) no		b) no
508	a) Yes	b) no		b) no
509	a) Yes	b) no		b) no
510	a) Yes	b) no		b) no
511	a) Yes	b) no		b) no
512	a) Yes	b) no		b) no
513	a) Yes	b) no		b) no
514	a) Yes	b) no		b) no
516	a) Yes	b) no		b) no
517	a) Yes	b) no		b) no
518	a) Yes	b) no		b) no

On participants profile

- Did your laboratory quantify PAHs in EDIBLE OIL before?
- If YES, for how long? (expressed in years) - If OTHER, please specify
- If YES, how many samples per year does your laboratory analyse for THIS FOOD CATEGORY? - If OTHER, please specify
- Is your laboratory accredited for the determination of PAHs in food?
- If YES, please specify the food matrix included in the accreditation scope - If OTHER, please specify - If you chose "the following of the matrices listed above", please report the corresponding codes
- If YES, please specify the PAHs included in the accreditation scope - If OTHER, please specify

NRLs

LabID	Analysis of PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
101	a) yes	c) 4-8	d) > 100	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8,	c) 15+1 EU priority PAHs
102	a) yes	c) 4-8	a) < 10	a) yes	6.1.1	c) 15+1 EU priority PAHs
103	a) yes	c) 4-8	b) 10-50	b) no	true	true
104	a) yes	d) 8-15	d) > 100	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8	c) 15+1 EU priority PAHs
105	a) yes	only previous proficiency test with LC-MS otherwise use of GC-MS for 4 years	a) < 10	a) yes	6.1.1.+6.1.2+6.1.3+6.1.4+6.1.6+6.1.7	15+1 EUpriority PAHs + acenaphthene, acenaphthylene,fluorene, fluoranthene, pyrene, anthracene, benzo(e)pyrene
106	a) yes	d) 8-15	a) < 10	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.7, 6.1.8	c) 15+1 EU priority PAHs
107	a) yes	c) 4-8	a) < 10	a) yes	6.1.1, 6.1.2, 6.1.3	b) 4 marker PAHs
108	a) yes	c) 4-8	a) < 10	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	c) 15+1 EU priority PAHs
109	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	c) 15+1 EU priority PAHs
110	a) yes	d) 8-15	c) 50-100	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	15+1 EU priority PAHs plus Phenanthrene, Anthracene, Pyrene, Fluoranthene, Benzo(e)pyrene
111	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3,6.1.4.6.1.7,6.1.8,	c) 15+1 EU priority PAHs
112	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.7, 6.1.8,	EU priority 15
113	a) yes	d) 8-15	a) < 10	a) yes	6.1.1	a) BaP
114	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2	b) 4 marker PAHs
115	a) yes	c) 4-8	c) 50-100	a) yes	6.1.1, 6.1.2, 6.1.3	a) BaP
116						
117	a) yes	a) <1	a) < 10	b) no		true
118	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	c) 15+1 EU priority PAHs
119	a) yes	e) >15	c) 50-100	a) yes	6.1.1 6.1.2 6.1.3 6.1.4	c) 15+1 EU priority PAHs
120	a) yes	d) 8-15	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	15+1 EU priority PAHs excluding Benzo(c)fluorene
121	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	24 PAHs including 15 EU priority PAHs (not accredited for Benzo(c)fluorene)

LabID	Analysis of PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
122	a) yes	d) 8-15	c) 50-100	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	28 PAHs including the above.
123	a) yes	d) 8-15	b) 10-50	a) yes	6.1.1	c) 15+1 EU priority PAHs
124						
515	a) yes	e) >15	d) > 100	a) yes	6.1.1	c) 15+1 EU priority PAHs

Food categories as listed in Regulation (EC) No 1881/2006:
Oils and fats (6.1.1)
Smoked meats and smoked meat products (6.1.2)
Muscle meat of smoked fish and smoked fishery products (6.1.3)
Muscle meat of fish (6.1.4)
Crustaceans, cephalopods, other than smoked (6.1.5)
Bivalve molluscs (6.1.6)
Processed cereal-based foods and baby foods for infants and young (6.1.7)
Infant formulae and follow-on formulae (6.1.8)
Dietary foods for special medical purposes (6.1.9)

OCLs

LabID	PAHs in Edible oil	For how long (years)	Samples / year	Accredited	Matrices in accreditation scope	Analytes in accreditation scope
501	a) yes	b) 1-4	a) < 10	b) no	true	true
502	a) yes	b) 1-4	c) 50-100	a) yes	6.1.1	c) 15+1 EU priority PAHs
503	b) no	true	true	a) yes	6.1.2	a) BaP
504	a) yes	b) 1-4	a) < 10	a) yes	foodstuffs, raw materials	e) other
505	a) yes	b) 1-4	a) < 10	a) yes	6.1.1.,6.1.2.,6.1.3.,6.1.4.	b) 4 marker PAHs
506	a) yes	c) 4-8	a) < 10	a) yes	6.1.2, 6.1.3	b) 4 marker PAHs
507	a) yes	c) 4-8	b) 10-50	a) yes	6.1.5	c) 15+1 EU priority PAHs
508	a) yes	c) 4-8	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	c) 15+1 EU priority PAHs
509	a) yes	e) >15	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3, 6.1.4, 6.1.5, 6.1.6, 6.1.7, 6.1.8, 6.1.9	c) 15+1 EU priority PAHs
510	a) yes	b) 1-4	c) 50-100	a) yes	6.1.1	b) 4 marker PAHs
511	a) yes	d) 8-15	c) 50-100	b) no	true	true
512	a) yes	b) 1-4	b) 10-50	a) yes	6.1.1	b) 4 marker PAHs
513	a) yes	b) 1-4	b) 10-50	a) yes	6.1.1, 6.1.2, 6.1.3,	b) 4 marker PAHs
514	a) yes	e) >15	b) 10-50	a) yes	6.1.1, 6.1.2,6.1.3,6.1.4,6.1.5,	b) 4 marker PAHs
516	a) yes	b) 1-4	b) 10-50	b) no	true	true
517	a) yes	c) 4-8	a) < 10	a) yes	6.1.1	e) other
518	a) yes	c) 4-8	c) 50-100	a) yes	6.1.7	e) other

Food categories as listed in Regulation (EC) No 1881/2006:
Oils and fats (6.1.1)
Smoked meats and smoked meat products (6.1.2)
Muscle meat of smoked fish and smoked fishery products (6.1.3)
Muscle meat of fish (6.1.4)
Crustaceans, cephalopods, other than smoked (6.1.5)
Bivalve molluscs (6.1.6)
Processed cereal-based foods and baby foods for infants and young (6.1.7)
Infant formulae and follow-on formulae (6.1.8)
Dietary foods for special medical purposes (6.1.9)

On the method applied

- How did you prepare the sample?
- Which extraction method did you use?
- Which was the MAIN purification step of your method?
- Which was the instrumental detection method you applied?
- Please describe the analytical column used
- Did you encounter any problems during the analysis of the sample?

NRLs

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
101	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	501 TP 54 GRACE 250 x 4,6 mm	b) No
102	a) Dilution	liquid-liquid extraction	a) Donor-Acceptor Complex Chromatography (DACC)	c) HPLC-FLD-UV	agilent zorbax eclipse plus c18 3.5µm 100X4.6mm	b) No
103	b) No preparation	b) Pressurized liquid extraction	c) Solid Phase Extraction (SPE)	c) HPLC-FLD-UV	Grace Vydac, C18 250x4.6 mm, 5um	b) No
104	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	Waters PAH C18, 5um, 3x250mm	b) No
105	addition of internal standard (ISTD)	d) No extraction	b) Size-Exclusion Chromatography	e) HPLC-MS	Zorbax Eclipse PAH 2.1x50mm, 1.8µ	Addition of ISTD at different concentration than calibration curve, corrected.
106	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	j) GC-MS	ZB-35, 30m, 0.25 mm i.d., 0.25 um	b) No
107	a) Dilution	d) No extraction	c) Solid Phase Extraction (SPE)	l) GC-MS/MS	Agilent Select PAH, 30 m, 0,25 mm, 0,15 µm	b) No
108	a) Dilution	d) No extraction	c) Solid Phase Extraction (SPE)	l) GC-MS/MS	Varian Select PAH, 30m x 0.25mm x 0.15 µm	b) No
109	a) Dilution	liquid/liquid-extraction	b) Size-Exclusion Chromatography	j) GC-MS	OPTIMA 35 MS, 30m; 0,25mm; 0.25 µm	b) No
110	liquid/liquid partition and SPE	liquied/liquid extraction	c) Solid Phase Extraction (SPE)	HPLC-FLD plus GC-MS	Select PAH, 30 m, 0.25 mm, 0.25 µ	Unclear FLD spectrum of chrysene obliged us to use an alternative technique. This may frequently occure in olive oils.
111	a) Dilution	d) No extraction	c) Solid Phase Extraction (SPE)	l) GC-MS/MS	SELECTPAH 15*0,15*0,10	b) No
112	b) No preparation	a) Saponification	d) Solvent partitioning	j) GC-MS	5% phenylmethyl 60m x 0.25mm x 0.25µ	b) No
113	a) Dilution	d) No extraction	SPE-MIP	j) GC-MS	DB 17 30m x 0.25mm x 0.15 um (50 % Phenyl) - methylpolysilossane	b) No
114	a) Dilution	liquid/liquid partitioning	c) Solid Phase Extraction (SPE)	j) GC-MS	Select PAH (30m×0,25mm×0,15µm)	b) No
115	Saponification, liquid/liquid extraction, chromatography/ fractionation	a) Saponification	d) Solvent partitioning	a) HPLC-FLD	LiChroCART 250-4, LiChrosper PAH (5µm)	b) No
116						
117	b) No preparation	b) Pressurized liquid extraction	c) Solid Phase Extraction (SPE)	l) GC-MS/MS	Varian GC Capillary column, Select PAH - 15m x0,15mm ID DF=0,10 um	b) No
118	b) No preparation	Liquid/liquid extraction with ACN/acetone	c) Solid Phase Extraction (SPE)	c) HPLC-FLD-UV	C18 (PAH specific), 250 x 4,6 mm, 5 um, Agilent PAH Pursuit	b) No

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
119	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	PAH C18 5um; 4,6x250mm, 5 µm (Waters P/N 186001265)	b) No
120	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	PAH C18, 5µm, 250 x 4.6 mm,	Apparently there is a discrepancy between the provided 4-PAH standard and our own 15+1 PAH standard. We have carrried out some recovery experiments and our conclusion was that the real concentrations of the provided 4-PAH standard were lower that the reported concentrations. The analysis of a RM of olive oil (FAPAS ref.T0636) gave recoveries of > 150 % when using the provided 4-PAH standard.
121	b) No preparation	a) Saponification	c) Solid Phase Extraction (SPE)	j) GC-MS	DB 35ms, 30m, 0.25 mm, 0.15µm	b) No
122	b) No preparation	a) Saponification	d) Solvent partitioning	j) GC-MS	PAH Select 30m (Varian)	b) No
123	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	k) GC-HRMS	Varian PAH-select, 30m x 0.25 mm x 0.15 µm and DB5-MS, 60 m x 0.25 mm x 0.25 µm	Suppression of benzo[a]anthracene signal on PAH-select column,for this PAH was therefor the DB5-MS column was used. No suppression problem with that column.
124						
515	c) Other	liquid-liquid extraction	c) Solid Phase Extraction (SPE)	j) GC-MS	SELECT PAH (30m x 0.25mm x 0.15um)	b) No

OCLs

LabID	Preparation	Extraction	Purification	Detection	Column	Problems
501	a) Dilution	a) Saponification	d) Solvent partitioning	j) GC-MS	Agilent DB-EUPAH; 20mx0,180mm*0,14µm	b) No
502	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	Reversed phase C18, 5µm, 150 x 4.6mm	b) No
503	b) No preparation	a) Saponification	d) Solvent partitioning	a) HPLC-FLD	LichroCHART 5µ 250 X 3mm	b) No
504	b) No preparation	liquid extraction	b) Size-Exclusion Chromatography	a) HPLC-FLD	Waters PAH C18 Column, 120Å, 5 µm, 4.6 mm X 250 mm	b) No
505	a) Dilution	d) No extraction	e) Other	a) HPLC-FLD	WATERS PAH (250mm x 4.6 mm x 5 um)	b) No
506	HCl hydrolysis	liquid-liquid extraction	e) Other	a) HPLC-FLD	Vudac Grase C18, 150x4.6mm 5um	b) No
507	LYOPHILISATION	EXTRACTION SOUS PRESSION TYPE ASE	c) Solid Phase Extraction (SPE)	l) GC-MS/MS	5% polysilarylène -95% polydimethylsiloxane 20M X 0.25mm x 0.25µm	b) No
508	b) No preparation	b) Pressurized liquid extraction	c) Solid Phase Extraction (SPE)	l) GC-MS/MS		b) No
509	b) No preparation	a) Saponification	b) Size-Exclusion Chromatography	l) GC-MS/MS	Select PAH (30mx250µmx0,15µm). Agilent	b) No
510	extraction	KOH; liquid to liquid	c) Solid Phase Extraction (SPE)	j) GC-MS	15m Varian Select PAH; 0,15 mm; 0,1 µm	b) No
511	b) No preparation	b) Pressurized liquid extraction	b) Size-Exclusion Chromatography	l) GC-MS/MS	TR-5MS length 30 m ID 0.25 mm film thickness 0.25 um	b) No
512	a) Dilution	d) No extraction	b) Size-Exclusion Chromatography	j) GC-MS	DB-EUPAH, 20 m, 0.180 mm, 0.14 µm	b) No
513	a) Dilution	d) No extraction	c) Solid Phase Extraction (SPE)	a) HPLC-FLD	Agilent Eclipse PAH 50x4.6mm 1.8um	b) No
514	a) Dilution	b) Pressurized liquid extraction	e) Other	a) HPLC-FLD	Lichrocard, PAH, 5um, 250-4mm	b) No
516	a) Dilution	SPE extraction	c) Solid Phase Extraction (SPE)	j) GC-MS	5%phenyl-95%dimethyl polixyloxane, 30 m x 0.25mm x 0.15um	b) No
517	a) Dilution	FILTER	e) Other	a) HPLC-FLD	Inertsil-P ODS-P 250 mm x 4,6 mm i.d, 5 um	b) No
518	a) Dilution	d) No extraction	a) Donor-Acceptor Complex Chromatography (DACC)	c) HPLC-FLD-UV	Varian Pursuit PAH	b) No

ANNEX 8: Data reported by participants

The data reported by the participants are compiled in the following tables. The results of replicate analyses together with the expanded measurement uncertainty (k=2) reported for the value for proficiency assessment are depicted in the graphs. Red lines indicate the thresholds for satisfactory z-scores.

Results reported by *NRLs* for the content of benz[*a*]anthracene (BAA) in the olive oil test material. Assigned value is 2.79 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
101	2,565	2,367	2,422	2,5	0,49
102	2,502	1,995	1,923	2,140	0,719
103	3,0	3,1	3,1	3,1	0,6
104	2,65	2,5	2,59	2,58	0,67
105	2,8	2,7	2,6	2,7	0,54
106	2,85	3,12	2,57	2,84	0,48
107	2,16	2,38	2,27	2,27	0,31
108	3,21	3,1	3,3	3,21	0,72
109	2,58	2,57	2,60	2,58	0,45
110	2,67	2,89	2,95	2,83	0,58
111	2,14	2,15	2,25	2,18	0,14
112	3,0	2,9	2,9	2,9	0,6
113	1,19	1,75	1,32	1,42	0,20
114	3,10	3,30	2,90	3,10	0,99
115	3,81	3,95	3,62	3,79	0,38
116	2,52	2,98	2,81	2,76	0,7
117	2,3	2,3	2,3	2,3	0,69
118	2,50	2,48	2,46	2,50	0,28
119	2,79	2,90	3,32	3,01	0,45
120	3,05	2,94	3,06	3,01	0,23
121	2,84	2,83	2,88	2,85	0,43
122	3,05	2,96	3,03	3,03	0,48
123	3,19	3,07	3,16	3,14	0,202
124	n.r.	n.r.	n.r.	2,84	0,1
515	2,2	1,8	2,2	2,1	0,9

n.r.: not reported

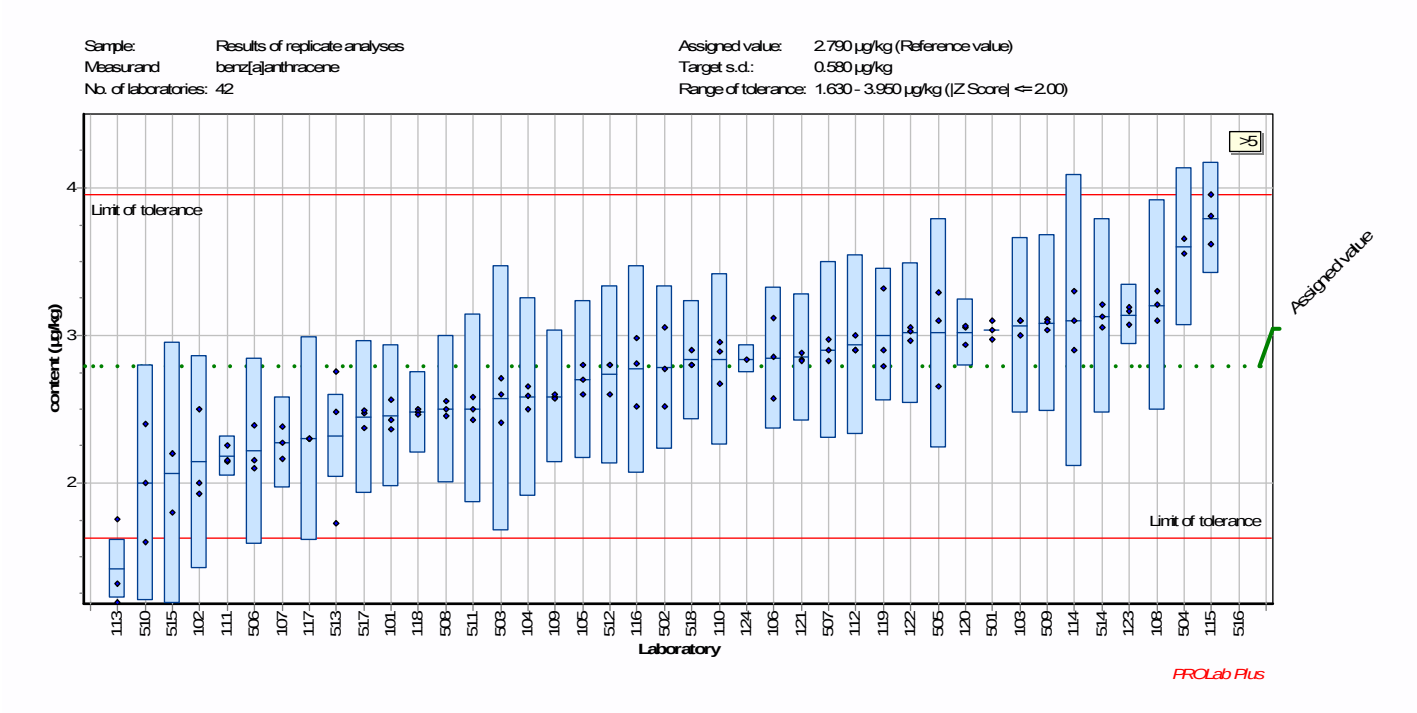
Results reported by *OCLs* for the content of benz[*a*]anthracene (BAA) in the olive oil test material. Assigned value is 2.79 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
501	3,04	3,1	2,97	3,037	0
502	3,057	2,515	2,771	2,781	0,5562
503	2,60	2,41	2,71	2,57	0,9
504	3,65	3,55	n.r.	3,6	0,54
505	2,65	3,10	3,29	3,01	0,78
506	2,39	2,15	2,10	2,21	0,63
507	2,83	2,97	2,90	2,90	0,60
508	2,45	2,55	2,50	2,5	0,5
509	3,11	3,09	3,04	3,1	0,6
510	1,6	2,4	2,0	2,0	0,8
511	2,43	2,50	2,58	2,5	0,64
512	2,6	2,8	2,8	2,7	0,6
513	1,73	2,48	2,75	2,32	0,28
514	3,05	3,13	3,21	3,13	0,66
516	5,32	5,37	6,06	5,58	0
517	2,47	2,37	2,49	2,44	0,52
518	2,8	2,8	2,9	2,8	0,4

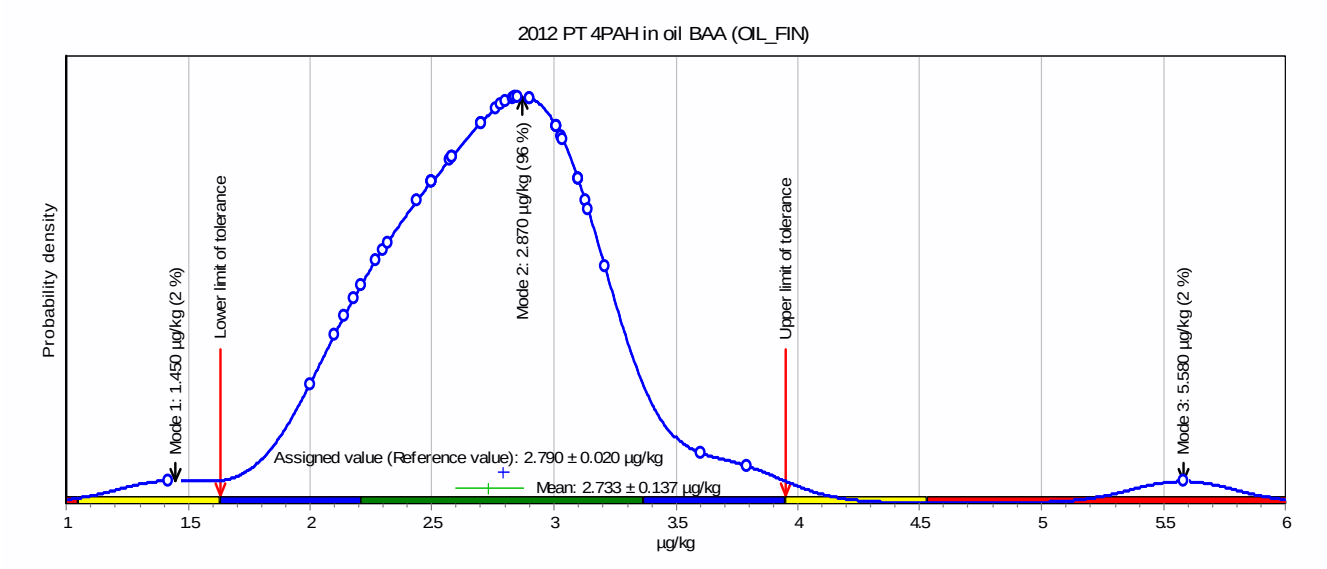
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benz[*a*]anthracene (BAA) content of the olive oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, red lines: lower and upper limit of satisfactory z-score range



Kernel density plot of the reported values for proficiency assessment for the benz[*a*]anthracene (BAA) content of the olive oil test sample



Results reported by *NRLs* for the content of benzo[*a*]pyrene (BAP) in the olive oil test material. Assigned value is 2.27 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
101	2,344	1,945	2,361	2,2	0,44
102	2,116	1,556	1,968	1,88	0,523
103	2,2	2,3	2,3	2,3	0,5
104	2,31	2,18	2,26	2,25	0,77
105	2,1	1,9	2,1	2	0,4
106	2,49	2,18	2,28	2,32	0,35
107	1,78	1,87	1,96	1,87	0,25
108	2,28	2,46	2,52	2,42	0,45
109	2,16	2,13	2,12	2,14	0,43
110	2,25	2,42	2,42	2,36	0,48
111	2,05	2,16	2,09	2,1	0,14
112	2,2	2,2	2,2	2,2	0,5
113	2,11	2,62	2,38	2,37	0,38
114	2,70	2,70	2,80	2,73	0,66
115	2,79	2,85	2,8	2,81	0,28
116	2,12	2,50	2,79	2,47	0,6
117	2,0	2,0	2,0	2,0	0,6
118	2,12	2,11	2,16	2,14	0,35
119	2,31	2,16	2,56	2,34	0,3
120	2,52	2,50	2,60	2,54	0,20
121	2,41	2,41	2,52	2,45	0,24
122	2,47	2,48	2,48	2,48	0,44
123	2,41	2,47	2,36	2,41	0,173
124	n.r.	n.r.	n.r.	2,17	0,2
515	1,8	1,5	1,7	1,7	0,7

n.r.: not reported

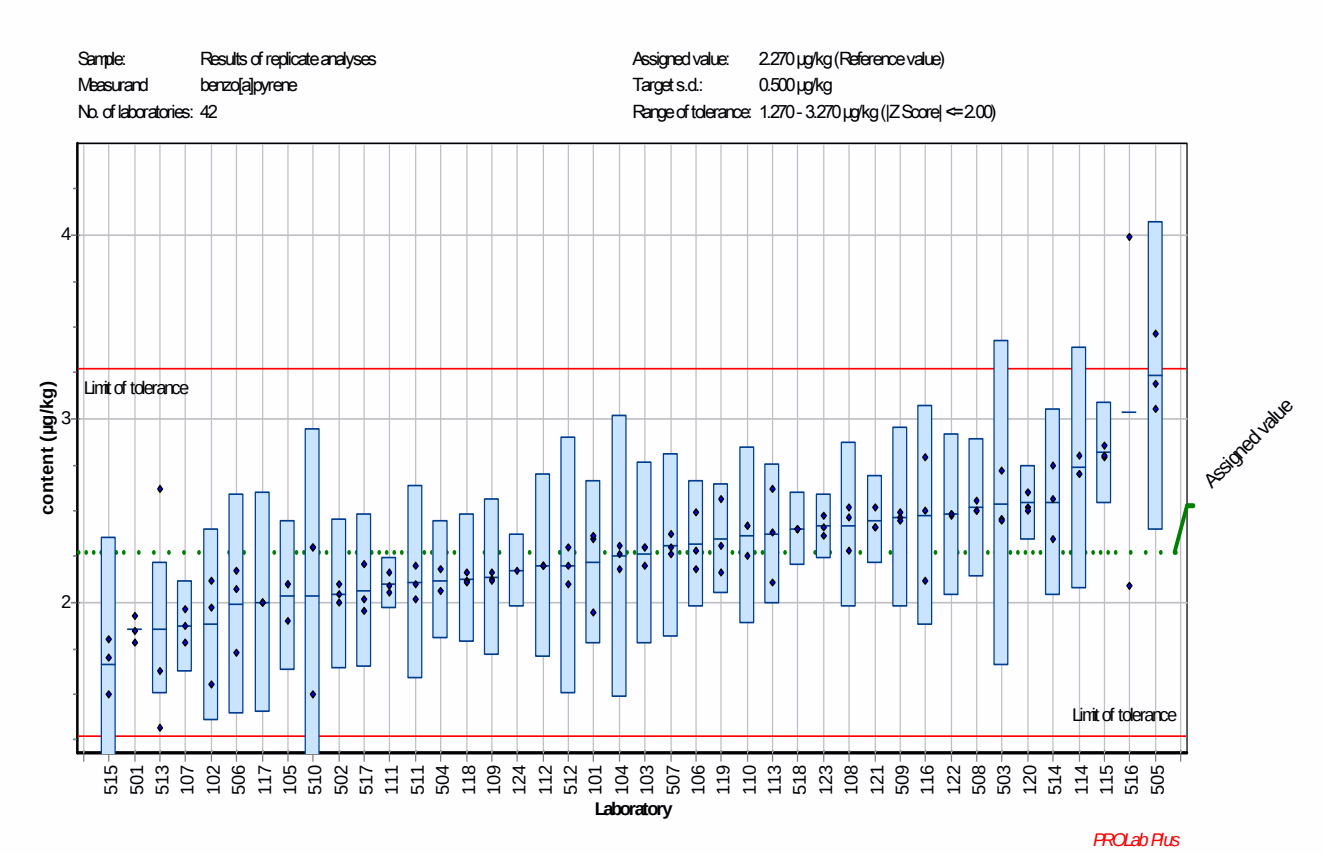
Results reported by *OCLs* for the content of benzo[*a*]pyrene (BAP) in the olive oil test material. Assigned value is 2.27 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
501	1,78	1,84	1,93	1,85	0
502	1,999	2,101	2,044	2,048	0,4096
503	2,45	2,44	2,72	2,54	0,89
504	2,06	2,18	n.r.	2,12	0,32
505	3,19	3,46	3,05	3,23	0,84
506	1,73	2,07	2,17	1,99	0,6
507	2,26	2,37	2,30	2,31	0,50
508	2,5	2,5	2,55	2,5	0,375
509	2,46	2,44	2,49	2,46	0,49
510	1,5	2,3	2,3	2,0	0,9
511	2,02	2,1	2,2	2,11	0,53
512	2,1	2,2	2,3	2,2	0,7
513	1,32	2,62	1,63	1,87	0,36
514	2,56	2,74	2,34	2,55	0,51
516	2,09	3,99	<10	3,04	0
517	1,95	2,02	2,21	2,06	0,42
518	2,4	2,4	2,4	2,4	0,2

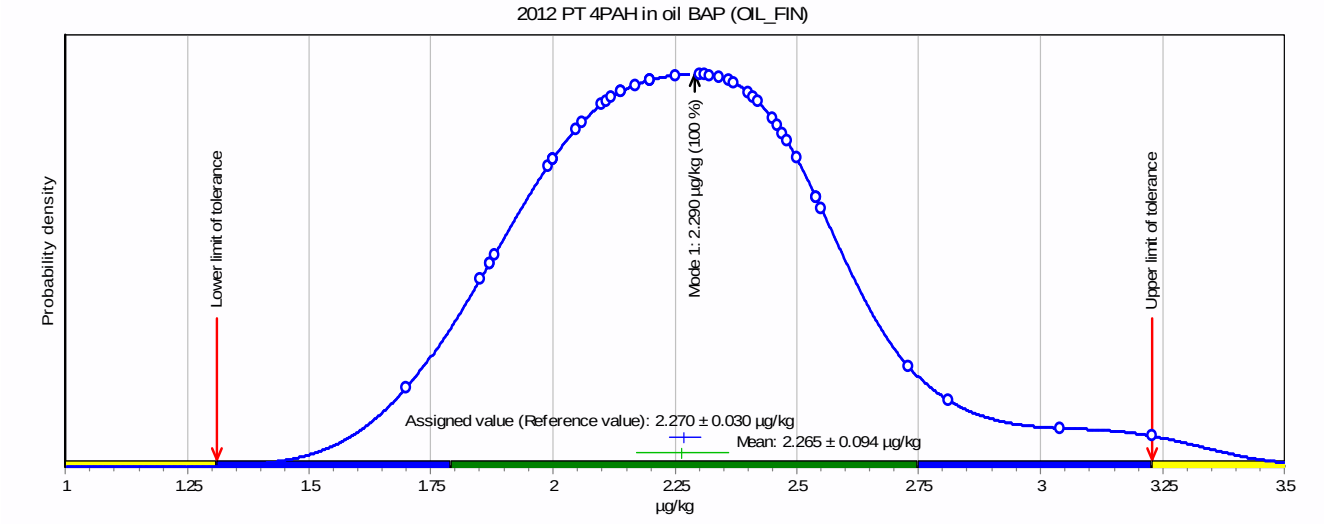
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*a*]pyrene (BAP) content of the olive oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, red lines: lower and upper limit of satisfactory z-score range



Kernel density plot of the reported values for proficiency assessment for the benzo[*a*]pyrene (BAP) content of the olive oil test sample



Results reported by *NRLs* for the content of benzo[*b*]fluoranthene (BBF) in the olive oil test material. Assigned value is 5.32 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
101	4,600	4,592	4,679	4,6	0,92
102	5,185	4,317	4,619	4,707	1,214
103	5,8	6,1	6,0	6,0	1,2
104	5,37	5,05	5,33	5,25	1,57
105	4,5	3,8	5,1	4,5	0,90
106	4,98	4,59	4,50	4,65	0,65
107	4,27	4,44	4,62	4,44	0,50
108	5,57	5,29	5,42	5,43	0,9
109	4,93	4,91	5,01	4,95	1,03
110	5,73	5,85	5,79	5,79	1,17
111	3,45	3,74	3,96	3,72	0,62
112	5,4	5,4	5,3	5,3	1,7
113	2,11	2,80	2,08	2,33	0,35
114	8,80	8,60	8,30	8,57	1,20
115	6,29	6,38	6,31	6,33	0,63
116	7,19	6,65	5,02	6,28	1,6
117	4,7	4,6	4,6	4,7	1,41
118	4,62	4,59	4,63	4,66	0,68
119	5,84	5,18	5,47	5,49	0,88
120	5,44	5,39	5,68	5,50	0,52
121	5,40	5,33	5,58	5,44	0,82
122	5,98	5,90	5,93	5,93	1,02
123	5,34	5,34	5,37	5,35	0,056
124	n.r.	n.r.	n.r.	5,13	0,4
515	4,4	3,6	4,3	4,1	1,7

n.r.: not reported

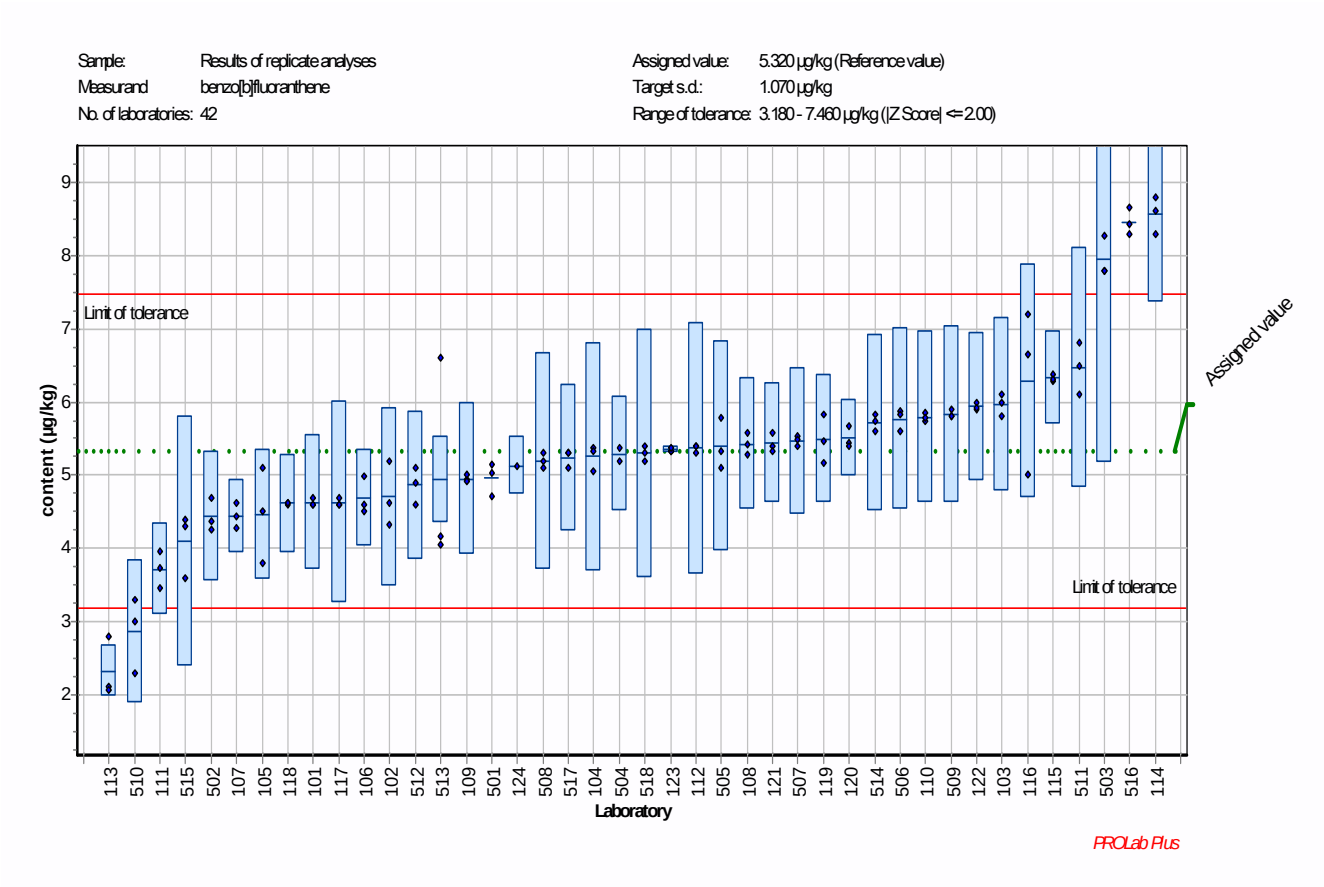
Results reported by *OCLs* for the content of benzo[*b*]fluoranthene (BBF) in the olive oil test material. Assigned value is 5.32 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
501	4,72	5,04	5,14	4,967	0
502	4,360	4,692	4,262	4,438	0,8876
503	8,27	7,78	7,78	7,94	2,78
504	5,20	5,37	n.r.	5,29	0,79
505	5,09	5,33	5,79	5,40	1,43
506	5,87	5,82	5,61	5,77	1,24
507	5,53	5,49	5,4	5,47	1,00
508	5,1	5,3	5,2	5,2	0,78
509	5,8	5,9	5,8	5,8	1,2
510	2,3	3,3	3,0	2,9	1,0
511	6,10	6,50	6,80	6,47	1,64
512	4,6	4,9	5,1	4,8	1,0
513	4,17	6,6	4,05	4,94	0,59
514	5,82	5,74	5,60	5,72	1,2
516	8,65	8,29	8,43	8,45	0
517	5,3	5,1	5,3	5,2	1,0
518	5,4	5,3	5,2	5,3	1,7

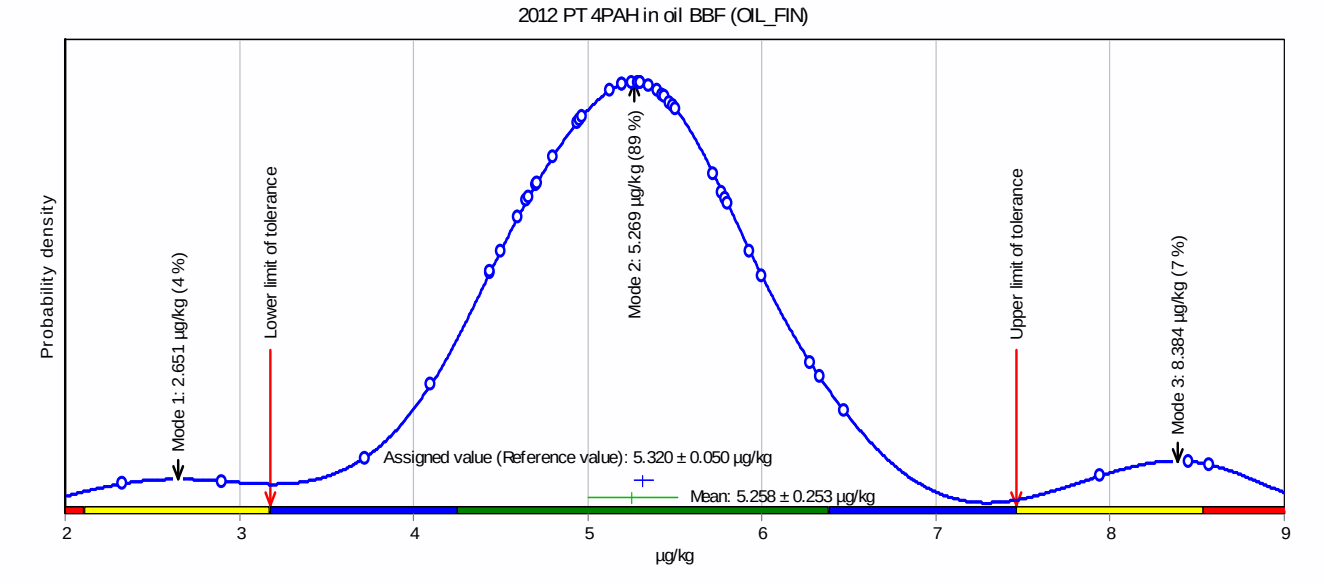
n.r.: not reported

Distribution of individual results of replicate determinations reported for the benzo[*b*]fluoranthene (BBF) content of the olive oil test sample

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, red lines: lower and upper limit of satisfactory z-score range



Kernel density plot of the reported values for proficiency assessment for the benzo[*b*]fluoranthene (BBF) content of the olive oil test sample



Results reported by *NRLs* for the content of chrysene (CHR) in the olive oil test material. Assigned value is 2.77 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
101	2,723	2,555	2,813	2,7	0,54
102	2,065	1,650	2,251	1,989	0,551
103	3,1	3,2	2,9	3,1	0,7
104	2,81	2,59	2,62	2,67	0,59
105	2,7	2,7	3,1	2,8	0,56
106	2,62	2,73	2,93	2,76	0,44
107	2,45	2,19	2,70	2,45	0,72
108	3,01	3,07	3,07	3,05	0,84
109	2,97	3,00	2,98	2,98	0,52
110	2,29	2,45	2,20	2,31	0,49
111	2,72	2,36	2,44	2,51	0,47
112	3,0	3,0	3,1	3,0	0,5
113	2,54	2,83	2,73	2,7	0,45
114	3,3	3,3	3,5	3,37	0,71
115	3,89	3,80	3,79	3,83	0,38
116	2,41	2,51	3,56	2,83	0,7
117	2,4	2,5	2,5	2,5	0,75
118	2,43	2,39	2,43	2,44	0,28
119	2,93	2,65	2,48	2,69	0,38
120	2,81	2,72	2,90	2,81	0,3
121	2,86	2,83	2,90	2,86	0,36
122	3,08	3,02	3,04	3,04	0,5
123	3,40	3,44	3,43	3,42	0,075
124	n.r.	n.r.	n.r.	3,30	0,2
515	2,2	1,8	2,2	2,1	0,9

n.r.: not reported

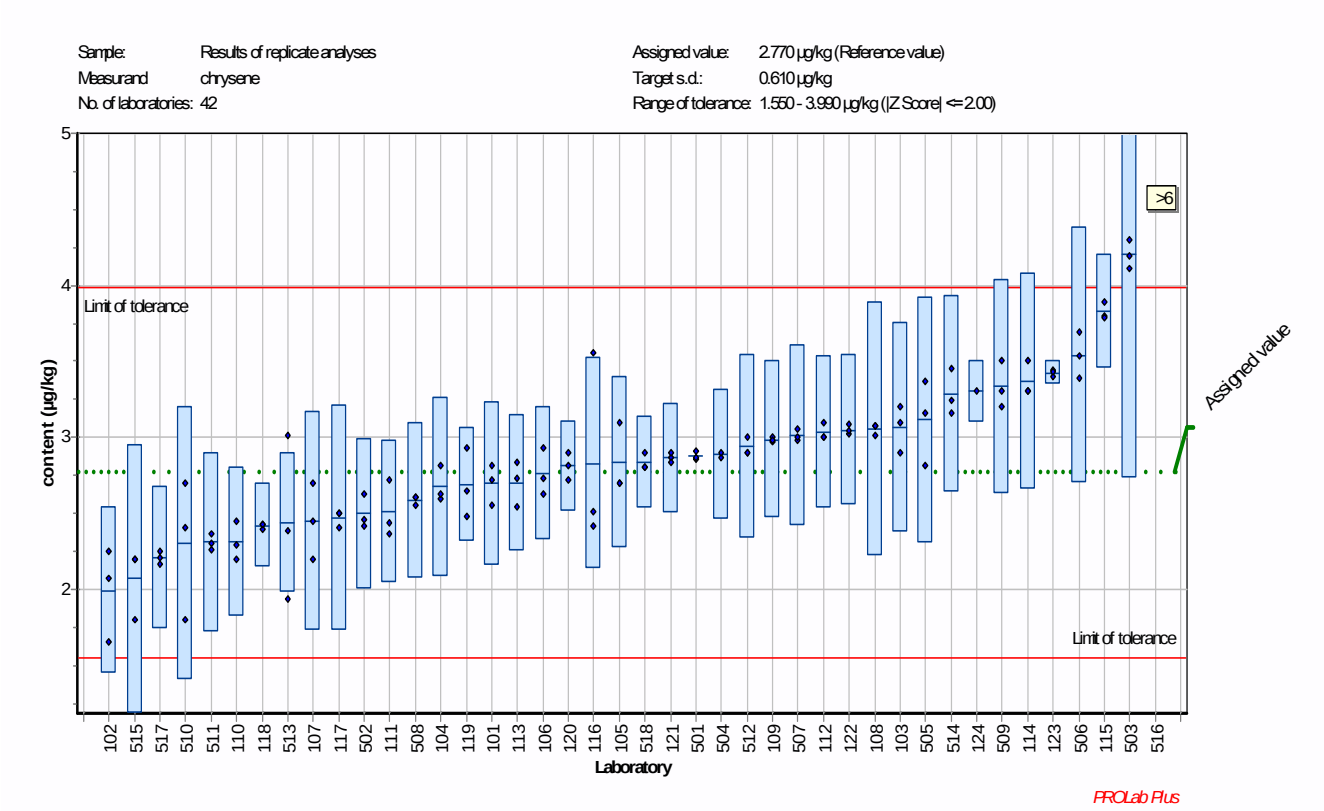
Results reported by *OCLs* for the content of chrysene (CHR) in the olive oil test material. Assigned value is 2.77 µg/kg

Lab code	Replicate 1 [µg/kg]	Replicate 2 [µg/kg]	Replicate 3 [µg/kg]	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
501	2,85	2,86	2,91	2,873	0
502	2,412	2,62	2,457	2,496	0,4992
503	4,11	4,19	4,30	4,20	1,47
504	2,87	2,90	n.r.	2,89	0,43
505	2,81	3,16	3,37	3,11	0,81
506	3,69	3,39	3,54	3,54	0,84
507	2,98	3,05	3	3,01	0,6
508	2,6	2,6	2,55	2,6	0,52
509	3,50	3,30	3,20	3,3	0,7
510	1,8	2,7	2,4	2,3	0,9
511	2,26	2,30	2,36	2,31	0,59
512	2,9	2,9	3,0	2,9	0,6
513	2,38	3,01	1,93	2,44	0,46
514	3,16	3,45	3,24	3,26	0,65
516	6,15	8,68	8,70	7,84	0
517	2,25	2,21	2,16	2,21	0,47
518	2,8	2,8	2,9	2,8	0,3

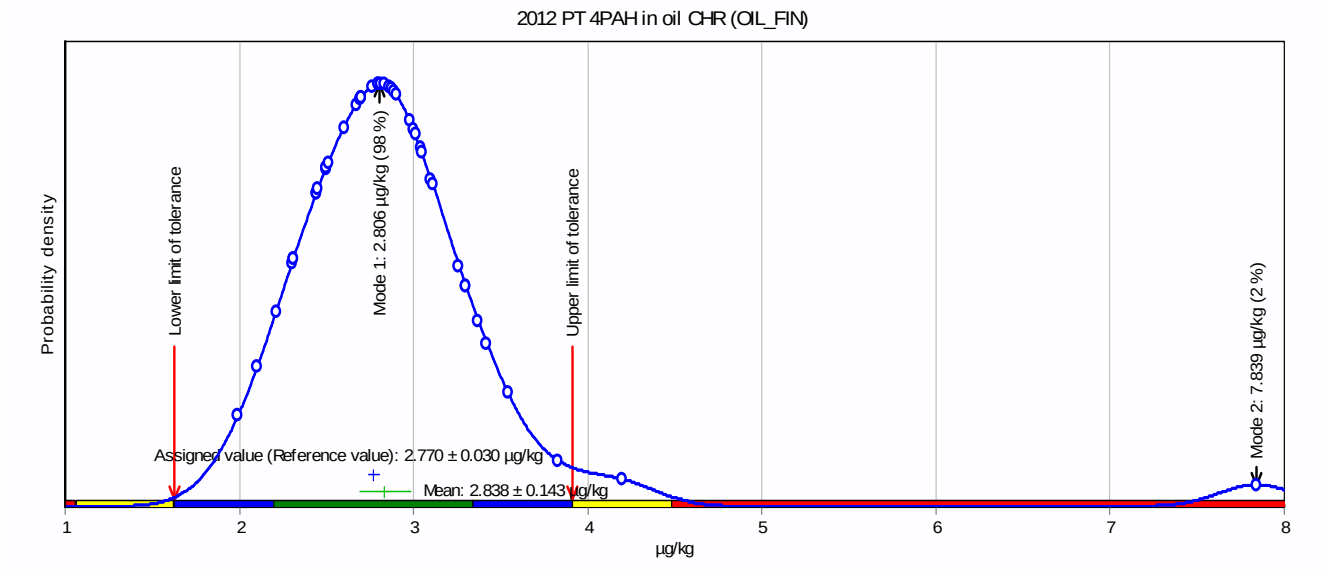
n.r.: not reported

Distribution of individual results of replicate determinations of chrysene (CHR) in the olive oil test sample.

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, red lines: lower and upper limit of satisfactory z-score range



Kernel density plot of the reported values for proficiency assessment for the chrysene (CHR) content of the olive oil test sample



Results reported by *NRLs* for the sum of the four marker PAHs (SUM) in the olive oil test material. Assigned value is 13.2 µg/kg

Lab code	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
101	12,0	1,3
102	10,716	3,007
103	14,5	1,6
104	12,75	1,97
105	12,1	1,2
106	12,57	2,14
107	11,03	0,96
108	14,1	2,83
109	12,65	4,82
110	13,30	1,47
111	10,5	0,8
112	13,5	1,9
113	8,82	0,71
114	17,77	1,83
115	16,76	0,88
116	14,34	3,6
117	11	6,6
118	11,73	2,06
119	13,53	3,94
120	13,86	0,67
121	13,60	1,02
122	14,48	1,31
123	14,33	0,282
124	13,4	1,3
515	10	4,2

n.r.: not reported

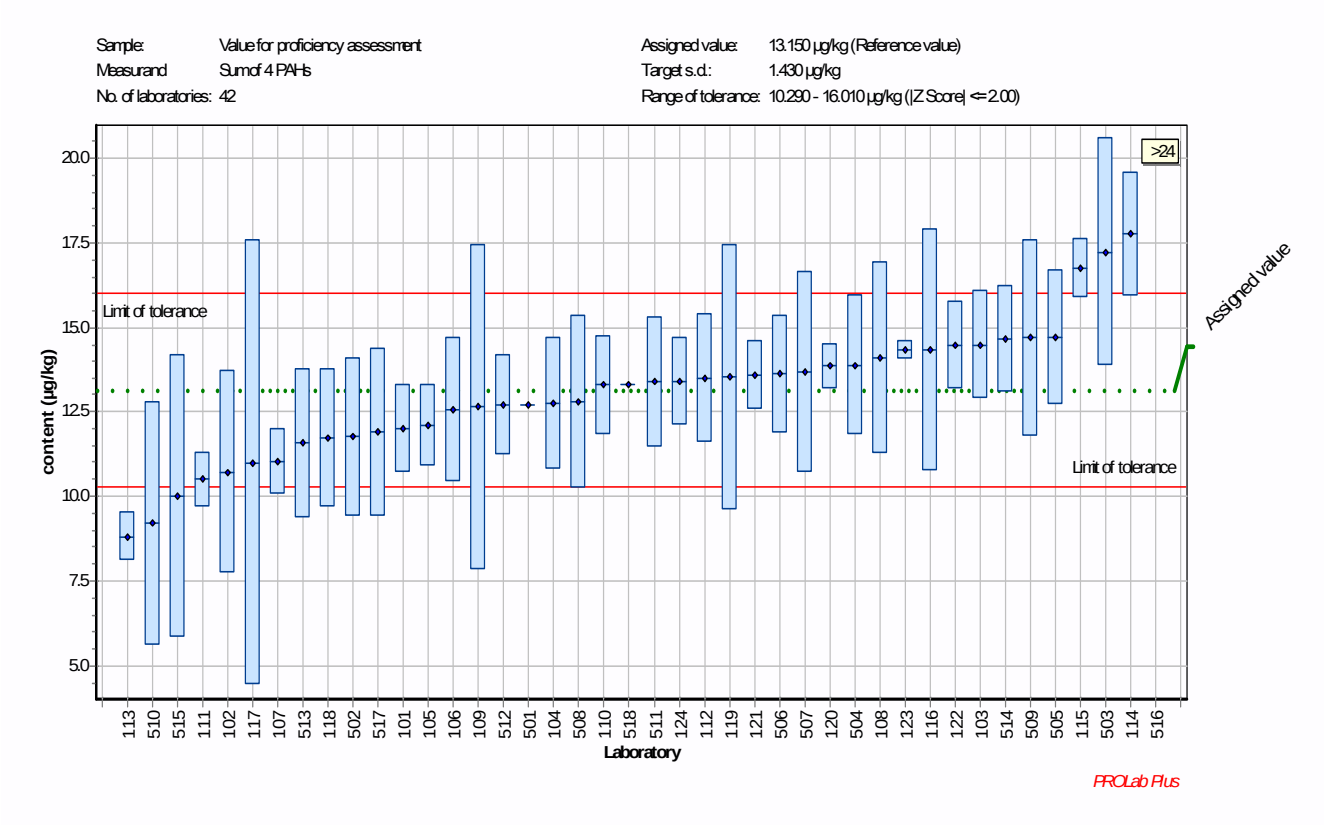
Results reported by *OCLs* for the sum of the four marker PAHs (SUM) in the olive oil test material. Assigned value is 13.2 µg/kg

Lab code	Value for proficiency assessment [µg/kg]	Uncertainty [µg/kg]
501	12,727	0
502	11,763	2,3526
503	17,25	3,39
504	13,89	2,08
505	14,72	2,00
506	13,62	1,73
507	13,69	3
508	12,8	2,56
509	14,7	2,9
510	9,2	3,6
511	13,39	1,93
512	12,7	1,5
513	11,57	2,2
514	14,66	1,6
516	24,91	0
517	11,9	2,5
518	13,3	n.r.

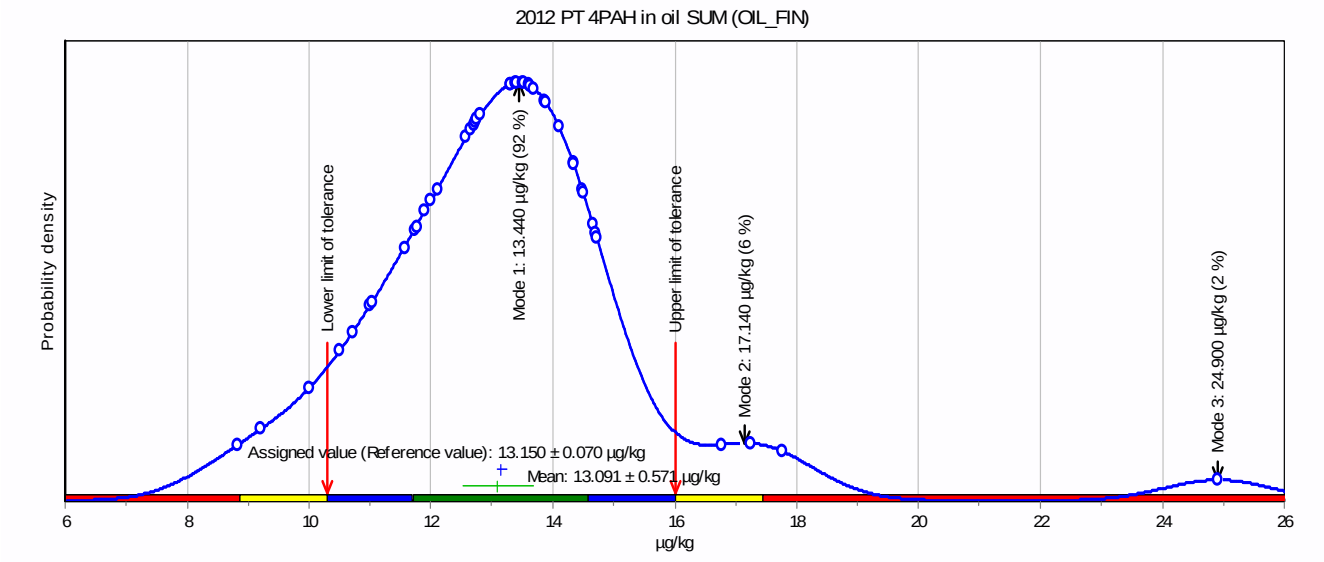
n.r.: not reported

Distribution of individual results of replicate determinations of the SUM of the content of the 4 PAH in the olive oil test sample.

blue triangles: individual results of replicate determinations, blue box: reported expanded measurement uncertainty (k=2), blue horizontal line in blue box: average of replicate determinations, green dotted line: assigned value, red lines: lower and upper limit of satisfactory z-score range



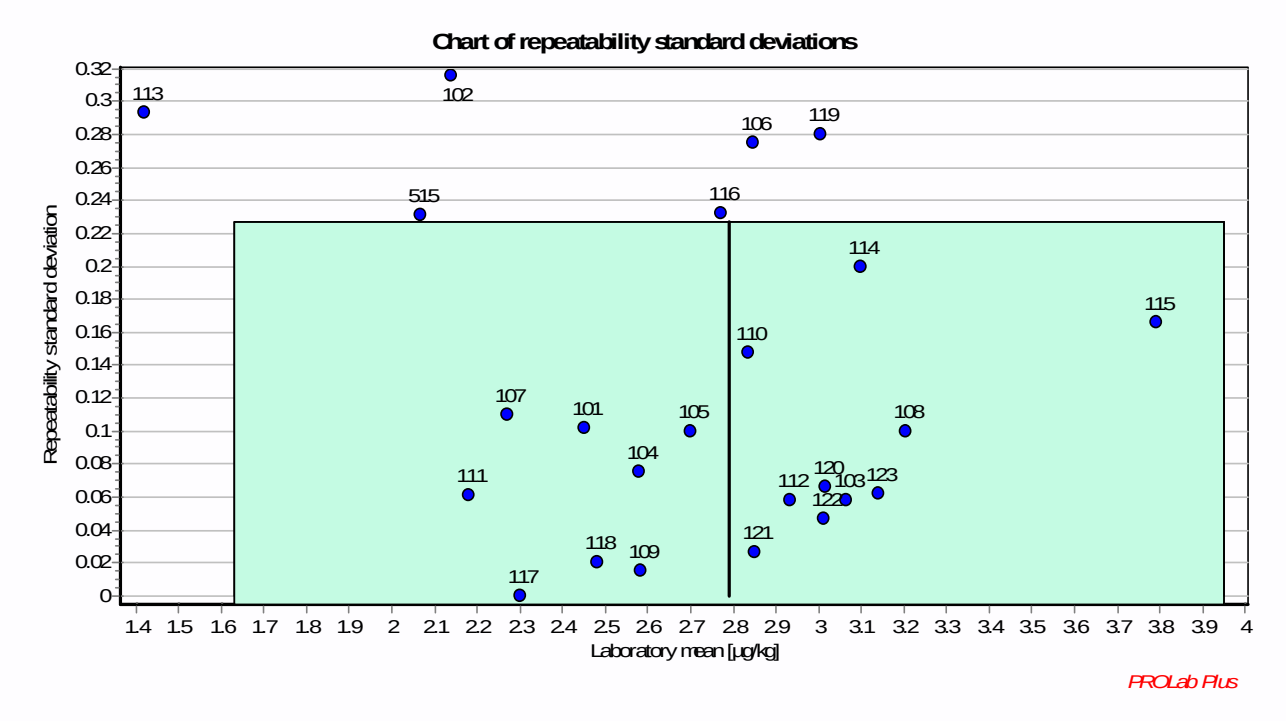
Kernel density plot of the reported values for proficiency assessment for the SUM of 4 PAH content of the olive oil test sample



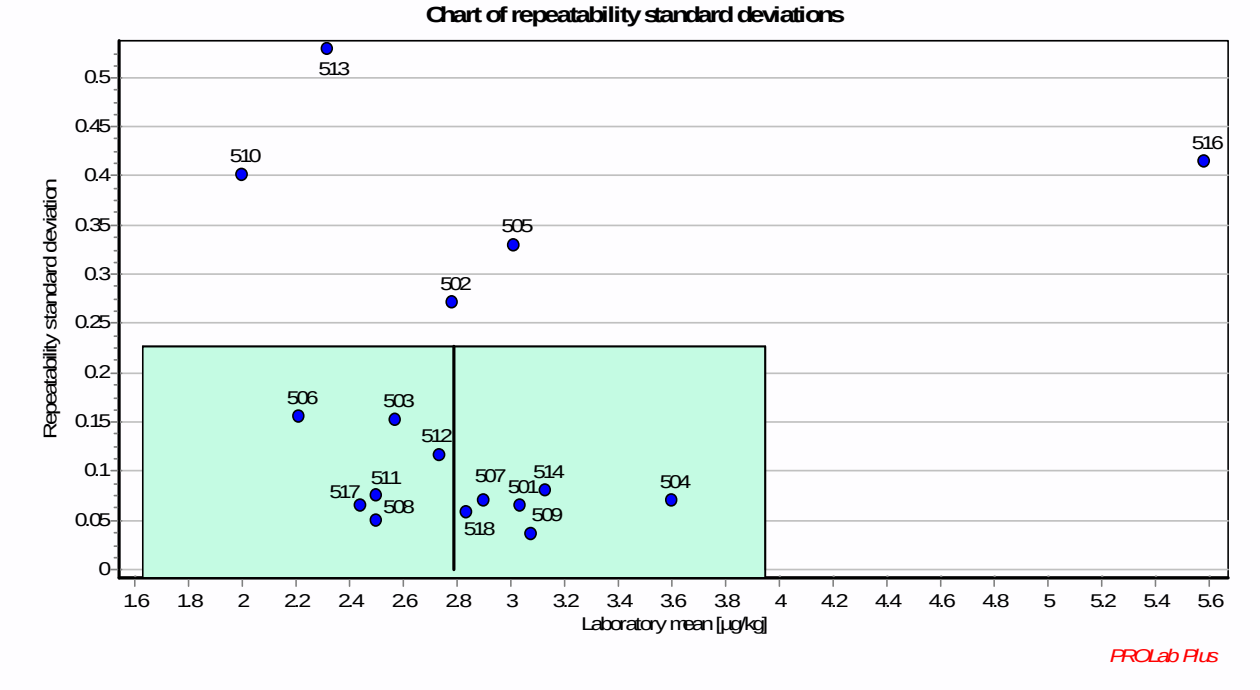
ANNEX 9: Laboratory means and repeatability standard deviation

Lab means and repeatability standard deviation for the determination of BAA in the olive oil test material

NRLs

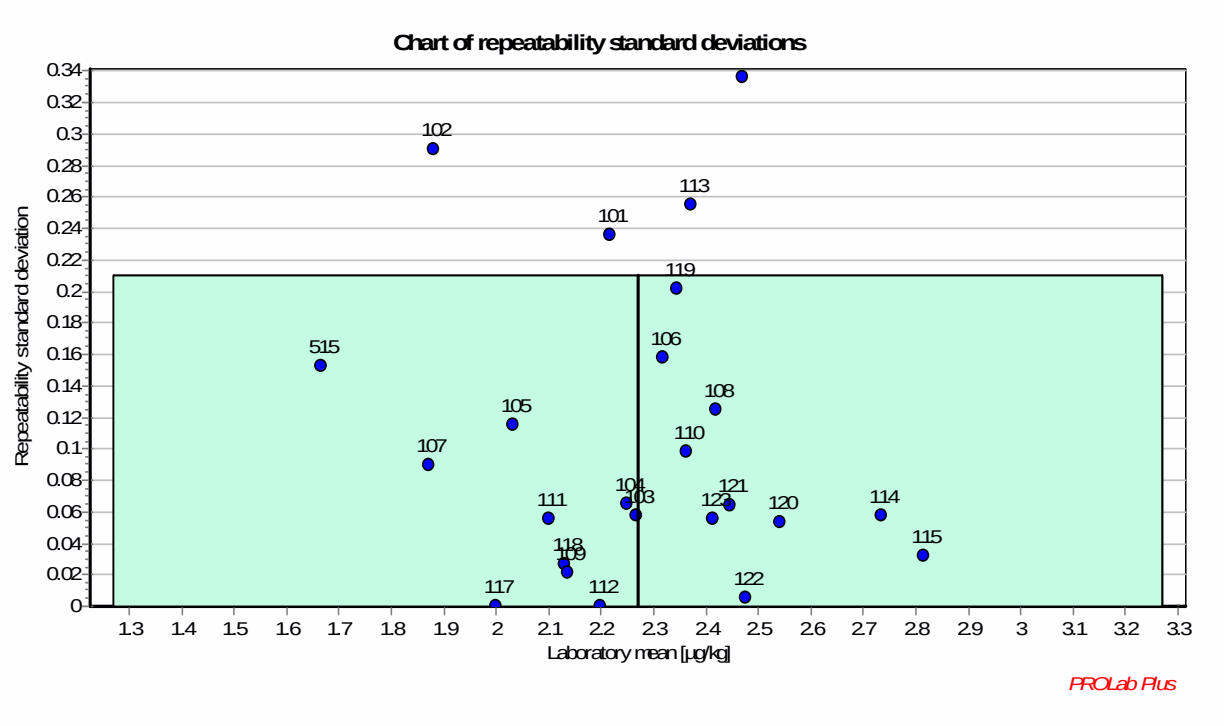


OCLs



Lab means and repeatability standard deviation for the determination of BAP in the olive oil test material

NRLs



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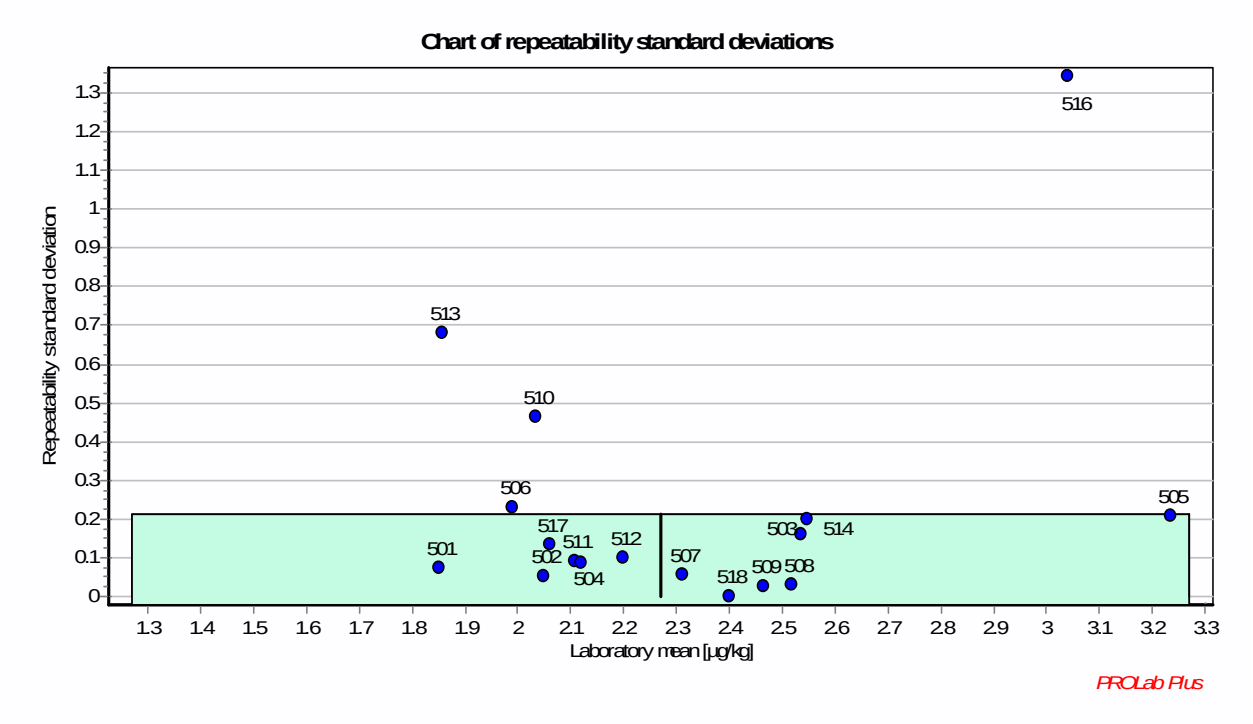
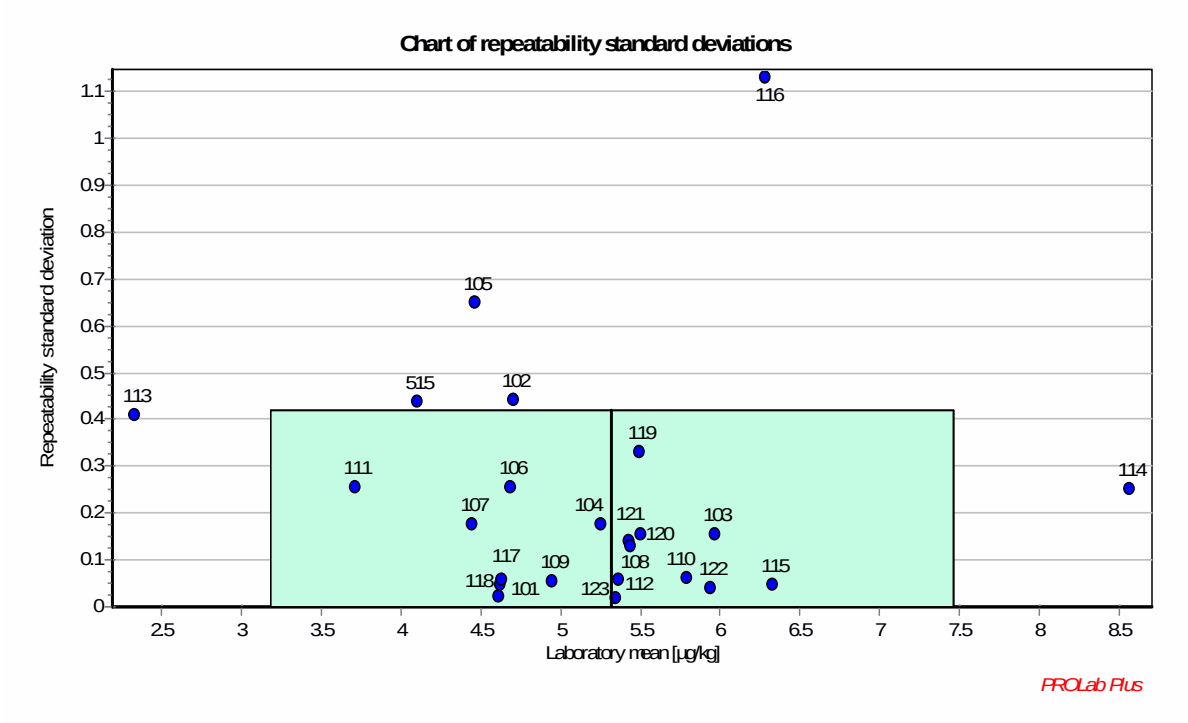


Lab means and repeatability standard deviation for the determination of BBF in the olive oil test material

NRLs



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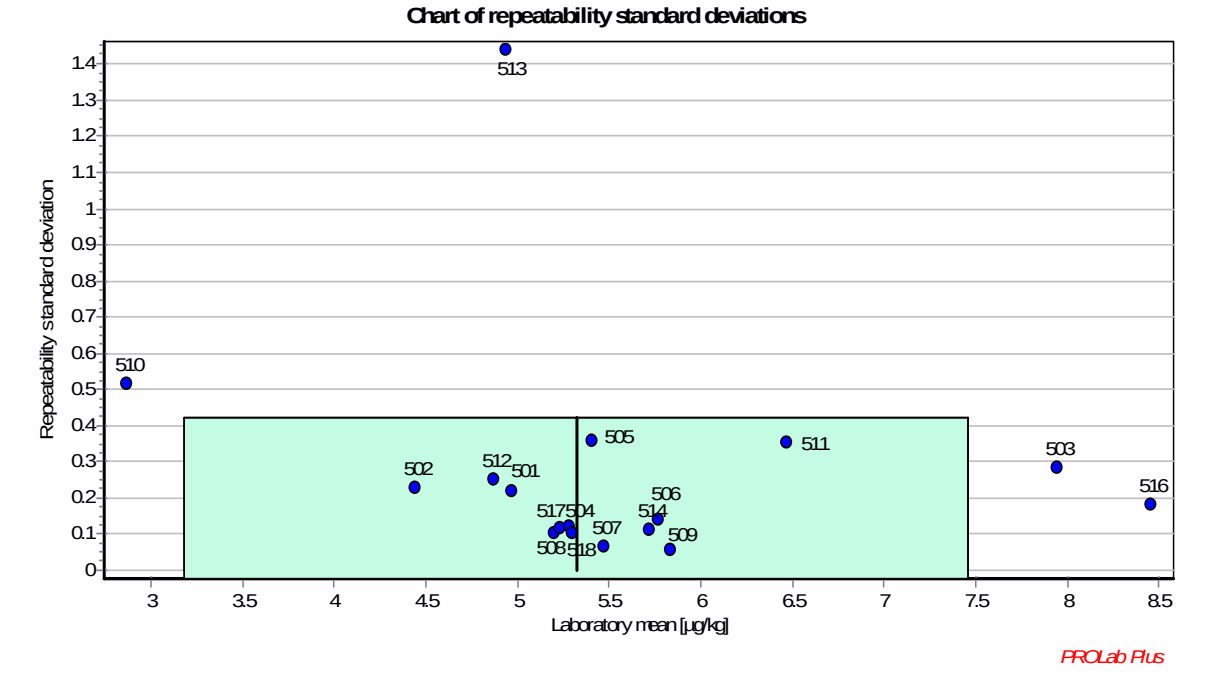
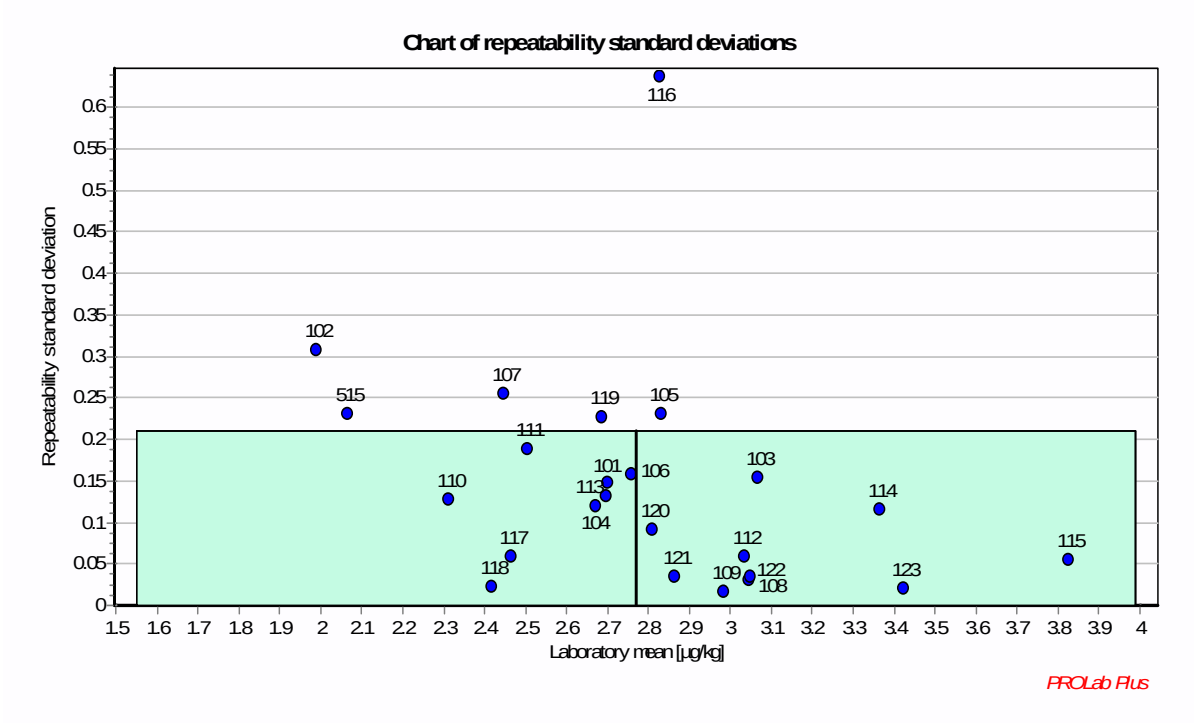
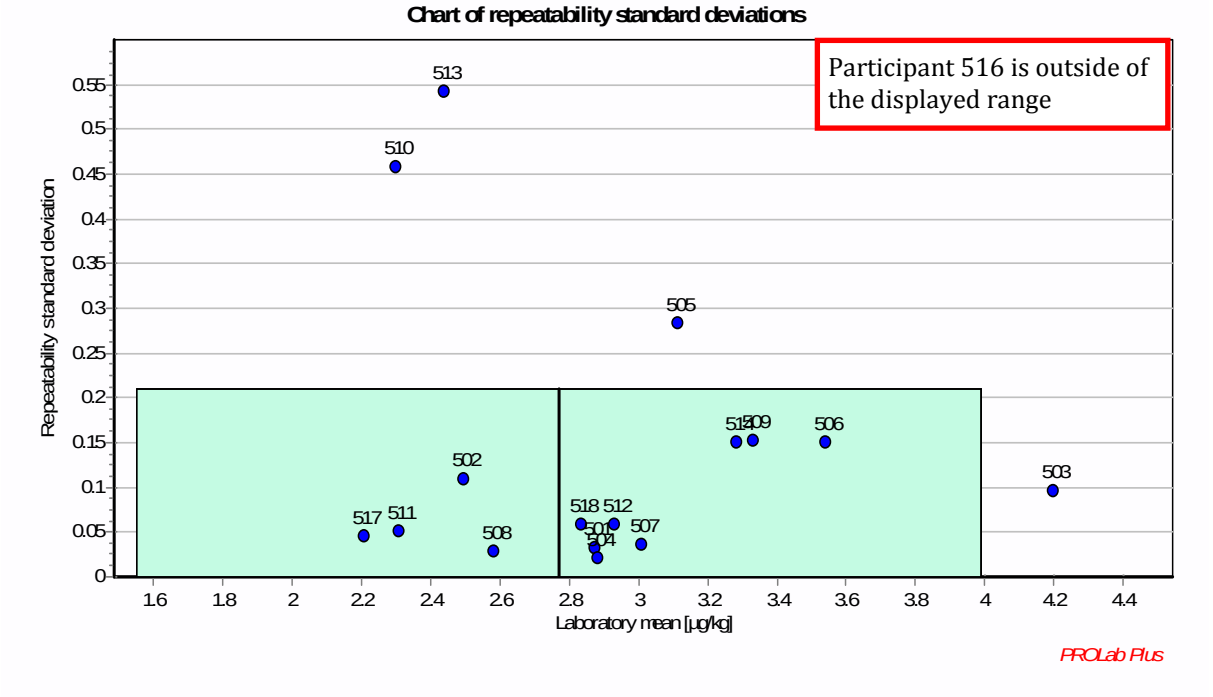


Lab means and repeatability standard deviation for the determination of CHR in the olive oil test material

NRLs



OCLs



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Authors: Stefanka Bratinova, Philippe Verlinde and Thomas Wenzl

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Abstract

The proficiency test here reported concerned the determination of the four marker polycyclic aromatic hydrocarbons (PAHs) in an olive oil test sample: benz[a]anthacene, benzo[a]pyrene, benzo[b]fluoranthene, and chrysene. Participants to these PT were National Reference Laboratories for PAHs (NRLs-PAHs) and EU official food control laboratories. The number of participants was 43. The PT was organised according to ISO Standard 17043:2010.

The test material used was olive oil spiked with the target PAHs. Participants also received a solution of the PAHs either in an organic solvent for checking their instrument calibration.

The results from participants were rated with z-scores and zeta-scores. About 94.4 % and 90.5 % of the results reported by NRLs and OCLs respectively were attributed with z-scores with an absolute value of below two, which is the threshold for satisfactory performance. The zeta-score ratings were worse, which indicates problems in the estimation of reliable measurement uncertainty values.

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